Information on Rice Pesticides
Submitted to the
Central Valley Regional Water Quality Control Board

December 28, 1994

by

J. Marshall Lee and Nancy N. Gorder

California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring and Pest Management Branch
Environmental Hazards Assessment Program
1020 N Street, Sacramento, California 95814-5624

SUMMARY

Department of Pesticide Regulation (DPR) staff reviewed the results of a program implemented by DPR in 1994 to reduce levels of five rice pesticides in surface water. The goal of the program was to meet performance goals for these pesticides, established by the Central Valley Regional Water Quality Control Board (Regional Board) to protect water quality and prevent toxicity. The five pesticides were the herbicides molinate and thiobencarb and the insecticides carbofuran, methyl parathion, and malathion. The most significant points of this review are:

- Rice acreage increased from 1993 by seventeen per cent: use of the herbicides was up and use of the insecticides was down.
- Concentrations of the five rice pesticides exceeded performance goals in at least one Sacramento Valley waterway during May and June.
- The most significant sources of rice pesticides concentrations in surface water appear to be aerial drift and seepage beyond the field perimeter.
- Water holding requirements used to facilitate dissipation of rice pesticides on the site of application appear to be adequate for meeting performance goals.
- Compliance with management practices for minimizing spillage of rice pesticides into surface water was good.
- Low flows in agricultural drainage canals provided minimal dilution of rice pesticides.
- Only three variances on water holding requirements (emergency releases) were approved; no obvious effects on pesticide concentrations were detected at monitoring sites.
- Mass loading of molinate in the Sacramento River and the Colusa Basin Drain was much lower than last year and was comparable to the estimates for 1992, the lowest year on record.
- Water collected periodically from the Colusa Basin Drain in May and June was not acutely toxic to aquatic invertebrates.

DPR proposed rice pesticide a program for implementation in 1995. The program includes management practices that will be reviewed by the Regional Board, who will rule on their adequacy in meeting performance goals, as required by the Regional Board's Water Quality Control Plan. The program has the same basic framework as the 1994 program, but will be strengthened as follows:

- Water management requirements for areas historically considered "geographically isolated" will be increased to better protect the Regional Board's water quality objective for toxicity.

- Management practices for containing seepage, and the pesticides it may contain, will be addressed through education and implemented through voluntary efforts.

- Drift control practices call special attention to potential problems associated with aerial applications to properties near agricultural drainage canals and deposition to sweat ditches, small drainage ditches used to channel seepage water away from a field's perimeter.

- DPR will investigate toxicity in closed irrigation systems in 1995.

- DPR will be responsible for the monitoring program, which will focus on a single site (the Colusa Basin Drain near SR 20).

The report also proposes that DPR prepare full reports for the Regional Board's review once every three years, rather than annually.

SUMMARY

Department of Pesticide Regulation (DPR) staff reviewed the results of a program implemented by DPR in 1994 to reduce levels of five rice pesticides in surface water. The goal of the program was to meet performance goals for these pesticides, established by the Central Valley Regional Water Quality Control Board (Regional Board) to protect water quality and prevent toxicity. The five pesticides were the herbicides molinate and thiobencarb and the insecticides carbofuran, methyl parathion, and malathion. The most significant points of this review are:

- Rice acreage increased from 1993 by seventeen per cent; use of the herbicides was up and use of the insecticides was down.
- Concentrations of the five rice pesticides exceeded performance goals in at least one Sacramento Valley waterway during May and June.
- The most significant sources of rice pesticides concentrations in surface water appear to be aerial drift and seepage beyond the field perimeter.
- Water holding requirements used to facilitate dissipation of rice pesticides on the site of application appear to be adequate for meeting performance goals.
- Compliance with management practices for minimizing spillage of rice pesticides into surface water was good.
- Low flows in agricultural drainage canals provided minimal dilution of rice pesticides.
- Only three variances on water holding requirements (emergency releases) were approved; no obvious effects on pesticide concentrations were detected at monitoring sites.
- Mass loading of molinate in the Sacramento River and the Colusa Basin Drain was much lower than last year and was comparable to the estimates for 1992, the lowest year on record.
- Water collected periodically from the Colusa Basin Drain in May and June was not acutely toxic to aquatic invertebrates.

DPR proposed rice pesticide a program for implementation in 1995. The program includes management practices that will be reviewed by the Regional Board, who will rule on their adequacy in meeting performance goals, as required by the Regional Board's Water Quality Control Plan. The program has the same basic framework as the 1994 program, but will be strengthened as follows:

- Water management requirements for areas historically considered "geographically isolated" will be increased to better protect the Regional Board's water quality objective for toxicity.

- Management practi for cont... ng seepage, and the pesticides it may contain, will be addressed th ugh education and implemented through voluntary efforts.

- Drift control practices call special attention to potential problems associated with aerial applications to properties near agricultural drainage canals and deposition to sweat ditches, small drainage ditches used to channel seepage water away from a field's perimeter.

- DPR will investigate toxicity in closed irrigation systems in 1995.

- DPR will be responsible for the monitoring program, which will focus on a single site (the Colusa Basin Drain near SR 20).

The report also proposes that DPR prepare full reports for the Regional Board's review once every three years, rather than annually.

TABLE OF CONTENTS

Department of Pesticide Regulation
Information on Rice Pesticides
Submitted to the Central Valley Regional Water Quality Control Board
December 28, 1994

Programs have been implemented by the Department of Pesticide Regulation (DPR) since 1983 to reduce discharges of the rice herbicides molinate (Ordram®) and thiobencarb (Bolero®) into surface waterways. In 1990, the objectives of these control efforts were clarified and expanded, following the adoption of amendments to the Central Valley Regional Water Quality Control Board's (Regional Board) Water Quality Control Plan (Basin Plan). This plan established performance goals for molinate and thiobencarb, beginning in 1990, and for the insecticides carbofuran (Furadan®), methyl parathion, and malathion, beginning in 1991.

The information provided reviews the factors affecting quantities of molinate, thiobencarb, carbofuran, methyl parathion, and malathion discharged to agricultural drains and the Sacramento River and efforts to meet 1994 performance goals. A summary of pertinent water quality monitoring efforts is also provided. Programs are proposed for implementation in 1995 that will help control discharges of molinate, thiobencarb, carbofuran, methyl parathion, and malathion from rice fields to levels that comply with the Basin Plan's performance goals and water quality objective for toxicity.

REVIEW OF 1994 PROGRAM

Discussion

A description of the 1994 rice pesticide program is presented in Appendix A. Program requirements were implemented by county agricultural commissioners using restricted material permits. The commissioner also provided information on the voluntary malathion program. A discussion of the 1994 rice pesticide program is presented below.

Molinate

The molinate program retained the water holding requirements that were in place since 1990. Treated water could be recirculated, discharged to fallow fields, or otherwise contained as long as it was not discharged from the system until the 29th day following the last application of molinate to water in the system. If the water in the system was under the control of one permit holder (e.g. contained in a single-grower recirculating system), treated water could be released from the site of application after label requirements (water held 4 days or until weeds were killed) were met. This allowed individual rice growers to manage water on their property with the maximum flexibility. In multi-grower systems which contain discharges from more than one permit holder (e.g. Reclamation District 108), individual permit holders could not discharge treated water into the system until the

9th day following application. The additional dissipation of molinate on the site of application provided by the additional holding requirement helped protect aquatic resources in the public waterways that are usually part of these multi-grower systems.

A provision of the molinate program, known as the emergency release provision, allowed molinate users to discharge treated water on an emergency basis before the end of the 28 day post-application holding period with the approval of the county agricultural commissioner. Such releases could occur as early as 12 days following application. Written requests were required and had to be submitted on the form provided in Appendix B. The requests included an inspection report written by a licensed pest control advisor demonstrated the rice crop was threatened by problems aggravated by the long holding requirement. Only enough water could be discharged to ameliorate the problem. A follow-up report (Appendix C) was required that indicated the time and duration of the emergency release and included information needed to calculate the total amount of water released during the emergency release.

Emergency releases in earlier years could occur as early as 7 days following application. Releasing field water so soon after application raised concern that such releases may be toxic. In fact, in 1993 the Regional Board exposed an aquatic invertebrate (Ceriodaphnia dubia) to samples of water released during emergency releases and found 100% mortality in almost all of the samples (Schnagl and Wyels 1993). As a result, the emergency release provision was made more restrictive; the minimum time between pesticide treatment and permissible emergency releases increased from 7 days to a length that should prevent acute toxicity in released field water. In the case of molinate, the minimum holding requirement prior to emergency releases increased to 11 days.

Thiobencarb

The thiobencarb program also retained the basic structure of earlier programs. The same program, implemented in 1991 and 1992, resulted in no detectable thiobencarb in the Sacramento River. In 1994, voluntary limits on sales of products containing thiobencarb, a part of the thiobencarb program since 1983, were eliminated. In 1993, the limits allowed for sales to accommodate the use of Bolero on 110,000 acres, and Abolish on 30,000 acres, in the watershed of the Sacramento River upstream of the "I" Street Bridge in Sacramento.

Carbofuran

The carbofuran program retained the basic strategies of the program used in 1993. For most fields, where carbofuran was incorporated into soil prior to flooding, permit conditions prohibited the discharge of water from fields to state waters for 28 days following flooding. In fields that were treated after field water was drained, the holding time began with the application. For most fields treated with carbofuran, the 28-day holding times were long enough to overlap with the holding times that follow molinate and thiobencarb applications. Thus, the program provided a carbofuran dissipation period of over a month in most cases.

As was the case in the molinate program, water from treated fields could be recirculated, discharged to fallow fields, or otherwise contained as long as it was not discharged from the system until the 29th day following the last application of carbofuran (or after the last preflood-treated field was flooded) in the system. Provisions for releasing water from the treatment sites in single- and multi-grower systems were the same as those described for molinate users.

As was the case with the molinate program, the emergency release provision was reevaluated for users of carbofuran in 1994. The dissipation and toxicological properties of carbofuran indicate that aquatic invertebrates are at risk whenever field water is released from a carbofuran-treated field prior to the end of the full 28-day holding time described in the program above. Thus, the emergency release provision was eliminated from the 1994 carbofuran program.

Methyl parathion

The basic methyl parathion program continued as it was since 1991: field water treated with methyl parathion had to be held on the site of application or within approved water management systems until the 25th day following application. The emergency release provision was also eliminated from the methyl parathion program, for the same reasons it was eliminated from the carbofuran program.

Malathion

As was the case since 1991, the program to reduce discharges of malathion to surface waterways was voluntary since malathion is not a restricted material and applications are not subject to use requirements or permit conditions. Information was provided to rice growers explaining the program when they obtained restricted material permits for other rice pesticides.

Seepage Control

Users of rice pesticides were required to prevent seepage of field water through the field's weir box, generally by securing the box with plastic and stacking soil to a depth higher than water level.

Drift control during aerial applications

Provisions addressing aerial drift of methyl parathion were strengthened in 1994. These provisions used the drift control measures outlined in section 6460 of Title 3 of the California Code of Regulations (Appendix D) as a basis, but additional measures were required to better prevent drift by further increasing the average size of spray droplets. They also prohibited applications to sites immediately upwind of waterways and to all sites when wind speeds were greater than five miles per hour. These practices were not thought to disrupt pest management in rice fields because methyl parathion readily disperses in field water and its efficacy is not dependent on even coverage.

Use of Selected Pesticides in 1994

In the rice-growing counties in the Sacramento Valley, county agricultural commissioners record the acreage treated with molinate, thiobencarb, carbofuran, and methyl parathion when Notices-of-Application (NOAs) are submitted to each county office. Based on these records, and on pesticide use reports where available, it was estimated that 385,302 acres were treated with molinate, 72,582 with thiobencarb, 148,189 with carbofuran, and 44,452 with methyl parathion (Table 1). These estimates indicate that molinate use increased approximately 5.7% over the use in 1993, thiobencarb use increased 16.2%, carbofuran use decreased 12.2%, and methyl parathion use decreased 20.9%. Pesticide use report data for other important rice pesticides, malathion and bensulfuron methyl (Londax®), are not available yet. About 485,000 acres of rice were grown in the Sacramento Valley in 1994, an increase of about 17% over 1993's crop.

Enforcement Activities

The county agricultural commissioners are responsible for the enforcement of the rice pesticide programs. The role of the commissioners and their staffs includes explaining the program to growers, pest control advisers and operators; issuing restricted material permits; inspecting fields for compliance; evaluating emergency release variances; and providing DPR with information on the use of pesticides.

Before any material on the list of California restricted materials may be applied, growers must obtain a permit from their county agricultural commissioner. The permits may specify conditions for use of the material, including post-application water holding requirements. A Notice-of-Intent (NOI) must be filed with the county agricultural commissioner 24 hours prior to the application, providing the commissioners with the option to observe the mixing, loading, and application of the material, thus enforcing regulations that pertain to pest control operations. Molinate, thiobencarb, carbofuran, and methyl parathion are currently California restricted materials; malathion is not. Permits which specify post-application water holding requirements, like those for the use of molinate, thiobencarb, carbofuran, and methyl parathion, also require that the NOA be filed within 24 hours after the application.

Staff of county agricultural commissioners and of DPR's Pesticide Enforcement Branch inspected about 1600 rice fields for compliance with water holding requirements. They cited 9 growers for holding time violations; four of which were determined to be unintentional (e.g. excessively leaky flash boards, etc.). Of the 9 violations, 3 were in Butte County, 5 in Colusa County, and 1 in Glenn County. Field inspectors noted the new provision requiring mounding of soil in front of each field's drain box was a very valuable enforcement tool. When drain boxes are bermed in this way, evidence of drainage through the box (e.g. during an illegal release of field water) is obvious.

Only county agricultural commissioners may grant variances on the holding requirements for fields treated with molinate if the length of the holding time was adversely affecting the rice plants. Those granted such variances were instructed to drain water only to the extent necessary to restore a healthy growing environment for the rice seedlings. In 1994, only three emergency releases, affecting a total of 172 acres, were issued. This is in contrast to the number issued in previous years. In 1990 and 1993, when rain in May and June overwhelmed the abilities of growers and irrigation districts to contain irrigation water, emergency releases affected 23,394 and 10,350 acres, respectively (Table 2). In 1991 and 1992, when unseasonable rain did not cause such problems, 2,224 and 1,029 acres, respectively, were discharged under emergency release variances. In 1994, a release of 75 acres was approved in Colusa County and releases of 25 and 72 acres were approved in Sutter County. Clearly, the more restrictive requirements for emergency releases reduced the number of growers qualifying for holding time variances.

Beginning in 1994, repeat and multiple violators will be required, as part of special permit conditions, to make improvements in their water management capabilities. Such improvements may include installation of pumps for tailwater recirculation or leaving land fallow to contain spillage. Growers who violate water holding requirements are subject to maximum penalties. However, conditions preceding violations (e.g. unfavorable field conditions that could not be moderated by the growers' best efforts) may be considered when assessing penalties.

Cooperative Water Quality Monitoring Program

Summaries of the monitoring activities addressing molinate, thiobencarb, carbofuran, methyl parathion, and malathion in Sacramento Valley waterways in 1994 are presented below. Locations of monitoring sites referenced in this report are presented in Figure 1. Their abbreviations can be interpreted as follows:

CBD1	Colusa Basin Drain at Roads 109 and 99E near Knight's Landing in Yolo County, near its outfall on the Sacramento River.
CBD5	Colusa Basin Drain near Highway 20 in Colusa County.
BS1	Butte Slough at Highway 20 in Sutter County.
SS1	Sacramento Slough at the Department of Water Resources gauge station in Sutter County, near its outfall on the Sacramento River.
SR1	Sacramento River approximately 1.5 km upstream from the confluence with American River, in Sacramento County.
SRRAW	Sacramento River at the intake to the water treatment facility in Sacramento, approximately 0.3 km downstream from confluence with American River, in Sacramento County.

Molinate and thiobencarb

Samples were collected twice weekly by the Department of Fish and Game (DFG); at CBD5 and BS1 from early May through early July and from CBD1 and SS1 from mid-

May to mid-June. Samples were delivered to Zeneca Ag Products, manufacturer of Ordram, for molinate analyses. Morse Laboratories of Sacramento performed thiobencarb analyses under contract with Valent, the primary distributor of products containing thiobencarb. Additional samples representing about 15% of the total collected were analyzed by the DFG laboratory for the presence of both compounds for quality assurance. Additional samples were collected and stored; they were analyzed when confirmation of analytical results was required. Blind spikes were periodically submitted for analysis with field samples.

The City of Sacramento analyzed water samples collected from the Sacramento River at the intake to its water treatment plant. Samples were collected on May 10 and twice weekly from May 23 through June 16.

Carbofuran, methyl parathion, and malathion

Samples were collected twice weekly by DFG at CBD5 and BS1 from early May through mid-June. Samples were delivered to FMC Corporation, manufacturer of Furadan, for carbofuran analyses and to the DFG laboratory for methyl parathion and malathion analyses. Additional samples representing about 25% of the total collected were analyzed for quality control: the DFG laboratory for carbofuran and the California Department of Food and Agriculture's (CDFA) laboratory for methyl parathion and malathion. Additional samples were collected and stored; they were analyzed when confirmation of analytical results was required. Blind spikes were periodically submitted for analysis with field samples.

Toxicity testing

Water samples were collected from the Colusa Basin Drain at CBD5 weekly from May 5 to June 13. DFG staff exposed neonate (<24 hours old) cladocerans (Ceriodaphnia dubia) to sample water for 96 hours, as well as to control water samples. Percent survival below that observed in the control samples was recorded.

Results of the 1994 Monitoring Program

Molinate

Concentrations of molinate in samples collected from agricultural drains are presented in Table 3. The Zeneca laboratory reported the highest concentration of molinate detected in these waterways in 1994 was 57 ppb in the Colusa Basin Drain (CBD5) on June 16. These data indicate the performance goal for molinate (10 ppb) was exceeded at each monitoring site except in Sacramento Slough. Table 4 presents the peak concentrations of molinate in Sacramento Valley waterways in each year since 1981.

The highest concentration of molinate detected in the Sacramento River was 0.42 ppb in a sample collected by the City of Sacramento at the intake to its water treatment facility on May 26 (Table 5). A peak of 1.7 ppb was found there in 1993. The maximum contaminate level, the level established to protect public health, for molinate is 20 ppb.

Thiobencarb
Analytical results reported by Morse Laboratories indicated thiobencarb concentrations in the agricultural drains were highest in the Colusa Basin Drain (CBD5) where they peaked at 37.4 ppb on May 16 (Table 6). Based on these results, the thiobencarb performance goal (1.5 ppb) was exceeded at both sites on the Colusa Basin Drain, but not at the sites on other agricultural drains. Table 7 presents the peak concentrations of thiobencarb in Sacramento Valley waterways in each year since 1981. The City of Sacramento did not detect thiobencarb in the Sacramento River (Table 5).

Carbofuran
Results of carbofuran analyses performed by FMC and DFG are presented in Table 8. The performance goal for carbofuran (0.4 ppb) was exceeded in the Colusa Basin Drain at CBD5, where a peak concentration of 2.3 ppb was detected. In 1994 the highest carbofuran concentration detected in the Sacramento Valley was 3.0 ppb, in the Colusa Basin Drain at CBD5.

Methyl parathion
Results of methyl parathion analyses performed by the DFG and CDFA laboratories indicated that the methyl parathion performance goal (0.13 ppb) was exceeded in the Colusa Basin Drain (Table 9). The highest concentration reported by DFG in this survey was 2.1 ppb, detected in a sample collected from CBD5 on June 9. The CDFA laboratory detected up to 1.40 ppb in these samples. The peak methyl parathion concentration in 1993, 1.1 ppb, was detected in a sample collected from Sacramento Slough.

Malathion
Analytical results indicated the malathion performance goal (0.1 ppb) was exceeded in the Colusa Basin Drain (CBD5) on June 9 when 0.32 ppb were detected (Table 10). In 1993, malathion was detected only once at CBD5, at a concentration of 0.15 ppb.

Toxicity testing
DFG staff found no statistically significant mortality in any of the toxicity tests (Fujimura 1994). Percent survival was slightly lower (80%) after exposure to water collected on June 13.

Quality assurance/control program
After reviewing the results of this program, it appears the results of the primary laboratories are valid and in general compare favorably to the split and replicate samples analyzed by the quality control laboratories. The quality control data are included in the tables listing results of the primary laboratories. All laboratories performed well on internal quality assurance and when provided with blind-spike samples. When there were discrepancies between the primary and quality control laboratories and when primary laboratories found unusually high concentrations, backup samples were analyzed (when available).

The DFG's sampling protocol was violated at least once, when low water levels at CBD5 made collecting water samples difficult using established techniques. After examining the nature of the violations and reviewing the general procedures used in the monitoring program, DPR determined the data developed during the program are valid (Appendix E).

Mass Transport of Pesticides in Agricultural Drains and the Sacramento River

Estimates of the total mass of pesticides transported in agricultural drains and the Sacramento River may be used to compare pesticide loading in different years. However, mass transport cannot be used to determine compliance with performance goals. The estimated mass transport of molinate in the Colusa Basin Drain at CBD5 is 819.8 lbs, a sharp decrease from the 1993 estimate (3414.3 lbs) and comparable to the 1992 estimate (682.1 lbs), the lowest on record. The values for the estimated transport of molinate in the Sacramento River past Sacramento were roughly proportional to those in the Colusa Basin Drain: 239.9 lbs in 1994, 4,232.4 lbs in 1993, and 124 lbs in 1992 (Table 11). Since thiobencarb was not detected in the Sacramento River in 1994, mass transport is assumed to have been zero.

Weather and Its Influence on Water Quality

Weather conditions, especially those during and after applications of rice pesticides, influence the performance of water quality control programs. Dissipation rates of many pesticides, e.g. molinate, increase with increasing temperature, so warm weather during water holding periods helps reduce concentrations. Warm weather in May of 1987 and 1992 helped explain why concentrations in waterways and mass transport in the Sacramento River were relatively low in those years. Conversely, in May 1990 and in late May and early June 1993, cool and rainy conditions prevailed, and the results of the molinate program were not as successful. Thus, it is important to be aware of weather patterns when reviewing monitoring data.

In 1994, weather was generally seasonable following pesticide applications, with the exception of a cool period in mid-May (Figure 2). Therefore, weather cannot account for any unusually high or low concentrations in area waterways. The 1993 weather pattern was not conducive to pesticide dissipation and the large number of emergency variances on water management requirements resulted in unusually high pesticide loading in the agricultural drains and the Sacramento River.

Flows in Agricultural Drainage Canals and the Sacramento River

Freshwater flows dilute pesticide-laden water that may enter surface waterways. But in 1994, the dilution capacity of regional agricultural drains, creeks, and the Sacramento River were very low due to drought. For example, the flows in Butte Slough were very low (Figure 3) and reflective of a dry Butte Creek, which in most years provides at least a four-to-one dilution effect for rice pesticides during May and June. Flows in the Colusa Basin Drain were also very low (Figure 4), almost eliminating discharges through the control gates at Knight's Landing to the Sacramento River. Growers who rely on the lower Drain as a source of irrigation water were without an adequate water supply. As was seen in 1993, a year in which seasonal runoff in the Sacramento Valley was relatively high, water conservation practices in rice-growing areas of Glenn and Colusa Counties resulted in minimal flows in the Drain in May and June when the presence of rice pesticides is most significant. Unless runoff from unseasonable rainfall increases flows, low flows in the Colusa Basin Drain, with minimal dilution capacity, will probably be the norm.

Sources of Pesticides in 1994

Pesticides used in rice culture may enter surface water from five sources under normal conditions. Drift during aerial applications and transport through levees with seepage water can be expected to contribute to loading during and shortly after the application period. Discharges from fields prior to the end of the legal holding times (i.e. illegal releases and emergency releases) are most prevalent two to four weeks following application. Legal releases are the predominant source of loading after the water holding requirements lapse. By examining the occurrence of rice pesticides in surface water in relation to their application schedules (Figures 5-9), presumptions can be made regarding the effects of each potential source.

Aerial drift

The 1994 rice pesticide program had specific provisions for reducing the effects of aerial drift on water quality, described above. However, evidence suggests that aerial drift accounted for brief, but significant contributions to pesticides detected in the Colusa Basin Drain. For example, on properties abutting the section of the Colusa Basin Drain immediately upstream from SR 20 (approximately 1.5 miles upstream of the CBD5 monitoring site, Figure 10), aerial applications of Abolish (the liquid formulation of thiobencarb) and methyl parathion were made within 18 hours of when monitoring detected high concentrations of these pesticides. Monitoring suggested that the effects of these incidents were brief, but accounted for the highest concentrations of thiobencarb and methyl parathion detected in 1994. An aerial application of Abolish in this same area (although not to a property immediately adjacent to the Drain) on June 1 may have contributed to the 4.0 ppb of thiobencarb detected at CBD5 on June 2. It is significant to note that flows in the Colusa Basin Drain on these dates were very low, as measured by the gauge at SR 20. Thus, the Drain had very little capacity to dilute contamination from aerial drift; the proximity of the applications to the monitoring site may not have provided sufficient time for other mechanisms to adequately dissipate the pesticides. There were no obvious sources of molinate and carbofuran that could be attributed to aerial drift from applications made immediately upstream of CBD5.

Seepage

In some rice fields, field water can move laterally through levees and beyond the perimeter of the field. Often levee borrow pits are used as a conveyance for this water (in this case known as "sweat ditches") and, when seepage flows are high enough, discharge the water into local drainage canal: 'olinate, apparently transported with this seepage, has been detected in water in sweat ies at concentrations as high as 840 ppb, even after the ditches were tarped to elimi. nfluences of aerial drift (Pino 1992). Staff of the Regional Board sampled four sweat ditches in 1994, although in this survey the ditches were not tarped. Molinate was detected in each ditch at concentrations ranging from 44 to 1300 ppb; carbofuran from 0.4 to 11 ppb. At one of the sites, molinate granules were visible on both sides of the sweat ditch, apparently the result of an inaccurate aerial application. Such aerial deposition of pesticides to sweat ditches is another means of transporting pesticides offsite into surface waterways.

In 1994, DPR staff attempted to better define areas where seepage helps sustain flows in agricultural drains. County Agricultural Department staff were asked to categorize seepage characteristics when they inspected rice fields for compliance with water management requirements. This information was entered into "Notice-of-Application" databases maintained by each county, along with other information that help county staff streamline enforcement efforts. Staff from DPR's Information Systems Branch is cooperating to link this database to the pesticide use permit database, which includes section/township/range coordinates for each rice field to which pesticides were applied. This exercise could ascribe a location to fields with each seepage category. Locations can be graphically displayed and should be useful in identifying local watersheds where seepage may contribute to pesticide loading.

The seasonal changes in molinate concentrations at CBD5 are more characteristic of sustained inputs like seepage than of the effects of incidental aerial drift, as was seen with methyl parathion and thiobencarb. Concentrations rose shortly after the application season began; this was well before sustained post-application drainage from rice fields could occur.

Emergency releases

The locations and dates of the releases did not correspond with unusual detections of pesticides at downstream monitoring sites.

Illegal releases

A review of monitoring results could not identify any effects these violations may have had to downstream water quality.

Legal releases

Evidence suggests that the length of the holding times in the Sacramento Valley is adequate to meet performance goals. After June 1, the approximate date on which the earliest post-application discharges may resume from treated fields, the presence of pesticides in regional waterways appears to be incidental and not characteristic of the sustained contamination expected from inadequate holding requirements. In most cases, performance goals during this period were not exceeded on two consecutive sampling dates, indicative of sources of contamination that are transitory, such as aerial drift from late season applications or illegal releases. Since the Colusa Basin Drain and Butte Slough had very low flows and thus low dilution capacities after June 1, any inputs with high concentrations of pesticides may not have been diluted to the degree necessary to meet performance goals. As was discussed earlier, this apparently was the case when applications of thiobencarb and methyl parathion contaminated the nearby Colusa Basin Drain. The highest concentrations of molinate in the Drain and Butte Slough occurred as incidental high values when flows in these waterways were minimal.

Additional information on thiobencarb

In 1994, the limitations on the sales of thiobencarb products were removed. Programmatic changes such as the berming of drainage structures and incentives for increasing the market share of Abolish 8EC were thought to be helpful in improving water quality overall and preclude the need for a sales limitation. Use information indicate thiobencarb use was within the limits defined by earlier sales limitations. In addition, results of the 1994 monitoring do not suggest the increased use of thiobencarb adversely affected water quality.

Concentrations of thiobencarb in the Colusa Basin Drain at CBD1 were inexplicably high from June 9 through 16. One potential source of thiobencarb was an emergency discharge of water from RD 108, a closed irrigation and drainage district, into the Colusa Basin Drain near the Colusa-Yolo County line. The discharges were made to supplement low Drain flows, thereby providing an emergency source of water to those who use the lower Colusa Basin Drain as an irrigation supply. RD108 monitored the Colusa Basin Drain before and during these discharges; the data indicate the discharges did not adversely affect water quality in the Drain and may have actually helped dilute pesticides already present in the Drain.

United Agricultural Products (UAP), distributors of Abolish, submitted data regarding the use of Abolish on fields where the "pin-point flood" method of water management, also known as the "Leather's method", is used. Such fields are flooded, then drained or allowed to dry soon after seeding to help promote root growth in the seedling. Abolish is then aerially applied and the field is reflooded. UAP's data show that thiobencarb concentrations are initially higher in field water treated in this manner, compared to fields treated with the "preflood surface" method (Heier and Sakamoto 1994). However, field concentrations appear to decline quickly so that by nineteen days, the last day of the Abolish holding time in most situations, concentrations are about the same as those in fields treated using the "preflood surface" method. It was demonstrated earlier (Valent 1993) that the potential for thiobencarb to be discharged from a field treated with Abolish 8EC using the preflood surface method was much lower than from a field treated with Bolero 10G.

1995 PROGRAM

Program Descriptions

In 1995, the rice pesticide program will continue to use restricted material permits and associated conditions to implement water management practices that reduce pesticide discharges into surface waters. In addition, management of other important sources of contamination will continue to improve. These practices, when fully implemented, are expected to result in attainment of water quality objectives and protect performance goals.

Molinate

I. All water treated with products containing molinate must be retained on the site of application for at least 28 days following application unless:

A. the treated water is contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 29 days following the last application of molinate within the system.

1. If the system is under the control of one permittee, treated water may be discharged from the application site in a manner consistent with product labeling.

2. If the system includes drainage from more than one permittee, treated water may be discharged from the application site into the system 9 days following application.

B. the treated water is on acreage within the bounds of areas that discharge negligible amounts of rice field drainage into perennial streams until fields are drained for harvest. All water on fields treated with molinate must be retained on the treated acreage until the 12th day following application.

II. Fields not specified in I.A. may resume discharging field water 29 days following application at a volume not to exceed two inches of water over a drain box weir. Unregulated discharges from these fields may then resume after 7 days.

III. The county agricultural commissioner may authorize the emergency release of tailwater 12 days following the last molinate application, following a review of a written request (Appendix B) which clearly demonstrates the crop is suffering because of the water management requirements. All water management requirements must be followed that are associated with other pesticides that may have been applied to the site. Additionally, the requester must describe preventative action that would avoid the need for future emergency releases. Under an emergency release variance, tailwater may be released only to the extent necessary to mitigate the documented problem.

Those issued an emergency release must submit to the county agricultural commissioner a report (Appendix C) indicating the time and duration of the emergency release and data that can be used to calculate the total amount of water released during the emergency release. Emergency release will only be granted for reasons related to rainfall, high winds, or other extreme weather conditions that cannot be moderated with management practices.

Thiobencarb

I. For rice fields treated with thiobencarb in the Sacramento Valley (north of the line defined by Roads E10 and 116 in Yolo County and the American River in Sacramento County), except those treated with Abolish 8EC:

A. All water on treated fields must be retained on the treated fields for at least 30 days following application unless:

1. The water is contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 20 days following the last application of thiobencarb within the system.

a. If the system is under the control of one permittee, treated water may be discharged from the application site in a manner consistent with product labeling.

b. If the system includes drainage from more than one permittee, treated water may be discharged from the application site into the system 7 days following application.

2. The water is on fields within the bounds of areas that discharge negligible amounts of rice field drainage into perennial streams until fields are drained for harvest. Water from such fields may be released 7 days after application if the county agricultural commissioner evaluates such sites and verifies the hydrologic isolation of the fields..

B. Fields not specified in I.A.1. and I.A.2. may resume discharging field water 31 days following application at a volume not to exceed two inches of water over a drain box weir. Unregulated discharges from these fields may then resume after 7 days.

II. For rice fields treated with thiobencarb in the Southern Area (south of the line defined by Roads E10 and 116 in Yolo County and the American River in Sacramento County), except those treated with Abolish 8EC:

A. All water on treated fields must be retained on the treated fields for at least 19 days following application unless:

1. The water is contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 20 days following the last application of thiobencarb within the system.

   a. If the system is und. the control of one permittee, treated water may be discharged from the application site in a manner consistent with product labeling.

   b. If the system includes drainage from more than one permittee treated water may be discharged from the application site into the system 7 days following application.

2. The water is on fields within the bounds of areas that discharge negligible amounts of rice field drainage into perennial streams until fields are drained for harvest. Water from such fields may be released 7 days after application if the county agricultural commissioner evaluates such sites and verifies the hydrologic isolation of the fields.

B. Fields not specified in II.A.1. and II.A.2. may resume discharging field water 20 days following application at a volume not to exceed two inches of water over a drain box weir. Unregulated discharges from these fields may then resume after 7 days.

III. For all areas, fields treated with Abolish 8EC:

A. All water on treated fields must be retained on the treated fields for at least 19 days following application unless the water is contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 20 days following the last application within the system.

   1. If the system is under the control of one permittee, treated water may be discharged from the application site in a manner consistent with product labeling.

   2. If the system includes drainage from more than one permittee, treated water may be discharged from the application site into the system 7 days following application.

B. Fields not specified in III.A. and III.B. may resume discharging field water 20 days following application at a volume not to exceed two inches of water over a drain box weir. Unregulated discharges from these fields may then resume after 7 days.

Carbofuran

I. Pre-flood applications of carbofuran to rice fields must be incorporated into the soil.

II. Water shall not be discharged from sites treated with carbofuran for at least 28 days following initial flooding (pre-flood application) or following application (post-plant application) unless the treated water was contained within tailwater recovery systems, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 29 days following the last application of carbofuran within the system.

A. If the system was under the control of one permittee, treated water may be discharged from the application site in a manner consistent with product labeling.

B. If the system included drainage from more than one permittee, treated water may be discharged from the application site into the system 9 days following application.

Methyl parathion

Water shall not be discharged from sites treated with methyl parathion for at least 24 days following application unless the treated water is contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system may discharge 25 days following the last application of methyl parathion within the system. Treated water may be discharged from the application site in a manner consistent with product labeling.

Malathion

The 1995 malathion program will be the same as the 1994 program. It is designed to maintain malathion discharges at low levels and help, along with efforts to minimize spray drift, to assure compliance with the performance goal of 0.1 ppb in Central Valley surface waters. The program will consist of a single practice: water should be held on the site of application for at least 4 days following application. Information addressing this voluntary program will be provided to rice growers by county agricultural commissioners.

Discussion

Water holding requirements

The water holding requirements in the Sacramento Valley in 1994 were adequate to meet performance goals and will not be adjusted in 1995. These holding requirements will continue to prevent acutely toxic discharges as well. However, to prevent acutely toxic discharges of pesticides in the southern Sacramento and San Joaquin Valleys, water holding requirements for most users of molinate and thiobencarb will increase. Water holding times will increase to allow the pesticides to dissipate to levels that are not acutely toxic (Harrington 1990). However, water holding times will not be increased in multi-grower closed systems. Rice growers in one of the several hydrologically isolated areas may not necessarily have increased holding times; the growers may request the county agricultural commissioner to evaluate, on a case-by-case basis, the characteristics of the local drainage system to determine whether discharged water has hydrologic continuity with perennial streams.

Drift Control

Drift control provisions will ' ıs they were in 1994, except special attent: will be given to prevent aerial depos ı to sw... ditches during applicati n.

Seepage

Seepage appears to make significant contributions to the pesticide load in local drainage canals. Concentrations of molinate and carbofuran have been high enough in sweat ditches to suspect that they are acutely toxic to aquatic invertebrates (Harrington 1990, Menconi and Gray 1992). Management practices are available that will help minimize these contributions and will be promoted as means to minimize pesticide movement with seepage.

Management practices include containment and reuse. Sweat ditches may be designed to hold more water, preventing the need for spillage, or to deliver the water to an area for ponding, such as unplanted acreage. The water may be delivered to other fields for reuse or pumped back into the field of origin. Any of the practices growers may use to help qualify for "closed status" are appropriate in minimizing discharges of pesticide laden seepage water.

DPR will work with county agricultural commissioners, irrigation districts, and the Natural Resources Conservation Service (formally the Soil Conservation Service) to educate growers on the potential adverse effects of discharged seepage and to promote voluntary implementation of practices that will help minimize these effects. The California Rice Industry Association has already pledged its support in this effort.

DPR, along with county agricultural commissioners, will continue its efforts to identify areas where seepage contributes to local water quality problems and will track voluntary efforts taken by growers to contain or reuse seepage water.

Emergency releases

No changes in the provisions for emergency releases are considered for 1995.

Education

As was the case in 1994, DPR staff will use opportunities to educate growers, pest control advisors, and applicators on the unique problems of rice pesticides and surface water contamination.

Enforcement

County agricultural commissioners will continue the enforcement program outlined above.

Studying toxicity in closed irrigation systems

DPR is planning a study to be conducted in 1995 on toxicity within closed systems to determine whether or not holding times must be increased to protect the water quality objective for toxicity. A draft protocol is attached (Appendix F).

Monitoring

DPR will assume the responsibility of planning and implementing the monitoring program in 1995. A draft monitoring protocol is attached (Appendix G). While the protocol only provides for monitoring one site (the Colusa Basin Drain at CBD5), it does not preclude DPR from sampling additional sites if conditions indicate a need. The City of Sacramento will continue to monitor its water intake on the Sacramento River for the presence of molinate and thiobencarb. DFG will continue to perform toxicity tests using water collected from CBD5.

Proposal for a three-year program

Annual reports addressing rice pesticides have been presented to the Regional Board since 1984. In this report, DPR presents management practices, that when fully implemented, should meet current performance goals. Therefore, annual reporting is not as imperative as it once was. The 1995 program is proposed as a three-year program: DPR will present a full report including an updated program for Regional Board review prior to the 1998 season. DPR will continue to prepare and submit to the Regional Board an annual summary of the monitoring data including an evaluation of the various sources of rice pesticides present in surface water. The program may be adjusted annually as necessary in response to unique patterns of pesticide concentrations revealed during the annual evaluation, but these adjustments will not require Regional Board approval. DPR will make programmatic adjustments when new water quality objectives are established, or if other legal guidelines are changed.

A triennial program review will provide time to develop, communicate, and coordinate any future programmatic changes, including careful thought and discussion among interested and involved parties. Staff at the Regional Board and at DPR will have time to address other priority surface water issues, rather than making minor adjustments to a largely successful program. This approach allows the county agricultural commissioner offices and the rice industry time to adjust to anticipated changes.

REFERENCES

Fujimura, R. 1994. Memorandum to Brian Finlayson, Department of Fish and Game: Aquatic toxicology laboratory report, results of examination (Aug. 8, 1994). Calif. Department of Fish and Game, Pesticide Investigations Unit, Elk Grove.

Harrington, J.M. 1990. Hazard assessment of the rice herbicides molinate and thiobencarb to aquatic organisms in the Sacramento River system. Calif. Dep. of Fish and Game, Environ. Services Div., Admin. Rep. 90-1, Rancho Cordova.

Heier, J.L. and S.S. Sakamoto. 1994. Rice field tailwater monitoring utilizing pin point flood cultural practice. United Agricultural Products.

Menconi, M. and S. Gray. 1992. Hazard assessment of the insecticide carbofuran to aquatic organisms in the Sacramento River system. Calif. Dep. of Fish and Game, Environ. Services Div., Admin. Rep. 92-3, Rancho Cordova.

Schnagl, R. and W. Wyels. 1993. Memorandum to Marshall Lee, Department of Pesticide Regulation: Molinate concentration in rice field discharges, 1993 (Aug. 6, 1993). Calif. Regional Water Qual. Control Board, Central Valley Region, Sacramento.

Valent. 1993. Abolish 8EC rice herbicide: proposal for inclusion into the 1993 rice pesticide control program (Feb. 10, 1993). Valent U.S.A. Corporation, Walnut Creek, CA.

Table 1. Acres treated with molinate (Ordram®)[1], thiobencarb (Bolero® and Abolish®), carbofuran (Furadan®), and methyl parathion in the counties of the Sacramento Valley in 1994[2].

County	Acres treated: molinate	thiobencarb	carbofuran	methyl parathion
Butte	82,665	6,237	41,919	1,907
Colusa	111,128	23,097	45,649	13,737
Glenn	70,384	7,645	13,945	2,142
Placer	10,315	4,949	6,733	2,208
Sacramento	7,808	4,120	2,735	1,478
Sutter	62,500	14,550	24,138	13,274
Tehama	1,226	0	218	0
Yolo	11,723	10,556	228	746
Yuba	27,553	1,428	12,624	8,960
Totals	385,302	72,582	148,189	44,452

1. Molinate may be applied more than once at each site.

2. Most values are based on Notices-of-Application submitted to county agricultural commissioners.

Table 2. Acres of molinate-treated rice fields where water was discharged under emergency release variances in the Sacramento Valley in 1987 - 1994

Year	Acres	Percent of total acres treated
1987	5,712	1.94
1988	4,897	1.41
1989	3,235	0.86
1990	23,394	6.32
1991	2,224	0.70
1992	1,029	0.29
1993	10,350	2.50
1994	172	0.04

Table 3. Molinate concentrations in Sacramento Valley waterways[1] in 1994[2].

	Molinate (ppb)				
Date	CBD1	CBD5		SS1	BS1
5/3	[3]	3.4			ND[4]
5/5		2.6	(2.6)[5]		ND
5/9		13			1.5
5/12		15	(11)		2.1
5/16	15	20		1.6	7.0
5/19	15	25	(17)	2.1	11
5/22	14	23		4.1	11
5/26	21	28	(18)	9.8	13
5/30	15	17		7.8	14
6/2	15.4	14.6	(16)	5.5	12
6/6	12	NR[6]		8.0	9.3
6/9	7.4	14	(11)	5.9	7.0
6/13	7.1	24		4.1	5.9
6/16	6.1	57	(11)	3.8	5.7
6/20		6.4			4.1
6/23		3.9			18.3
6/27		7.8			4.2
6/30		7.3	(6.6)		3.3
7/4		12.4			2.8
7/7		4.5	(4.7)		1.8

1. CBD1 Colusa Basin Drain at Roads 109 and 99E near Knight's Landing in Yolo County.
   CBD5 Colusa Basin Drain at Highway 20 in Colusa County.
   SS1 Sacramento Slough at DWR gauge station in Sutter County.
   BS1 Butte Slough at Highway 20 in Sutter County.

2. Samples collected by the California Department of Fish and Game (CDFG) and analyzed by Zeneca Ag Products.

3. Blanks indicate site was not sampled.

4. ND None detected, method detection limit = 1.0 ppb.

5. Values in parentheses are results of analyses performed on replicate samples by the CDFG Water Pollution Control Laboratory, Rancho Cordova. Method Detection Limit = 0.5 ppb.

6. NR Not reported.

Table 4. Peak molinate concentrations in selected Sacramento Valley waterways[1] in 1981 - 1994

	Concentration (ppb)				
Year	CBD1	CBD5	SS1	BS1	SR1
1981	340	357	[2]		
1982	204	697		187	27
1983	211	228	68		7
1984	110	120	44		21
1985	95	100	49		16
1986	77	88	30		11
1987	43	53	22	44	7.6
1988	67	89	30	52	8.0
1989	51	60	30	43	6.0
1990	51	59	40	36	8.9
1991	18	17	9.6	26	1.3
1992	6.2	24	15	26	ND[3]
1993	69.1[4]	96.1	31.2	39.2	2.59
1994	21	57	9.8	18.3	

1. CBD1 Colusa Basin Drain at Roads 109 and 99E near Knight's Landing in Yolo County.
   CBD5 Colusa Basin Drain at Highway 20 in Colusa County.
   SS1 Sacramento Slough at DWR gauge station in Sutter County.
   BS1 Butte Slough at Highway 20 in Sutter County.
   SR1 Sacramento River at Village Marina in Sacramento County.

2. Blanks indicate no data are available.

3. ND None detected. Method detection limit = 1.0 ppb.

4. Mean of duplicate analyses.

Table 5. Concentrations of molinate and thiobencarb in the Sacramento River at the intake to the City of Sacramento water treatment facility (SRRAW) in 1994[1].

Date	Concentration (ppb) molinate	Concentration (ppb) thiobencarb
5/10	ND[2]	ND
5/23	ND	ND
5/26	0.42	ND
5/30	0.27	ND
6/02	0.29	ND
6/06	0.31	ND
6/09	0.34	ND
6/13	ND	ND
6/16	ND	ND

1. Samples collected and analyzed by the City of Sacramento.

2. ND None detected. Limit of detection = 0.10 ppb.

Table 6. Thiobencarb concentrations in Sacramento Valley waterways[1] in 1994[2]

Date	CBD1	CBD5		SS1	BS1
	Thiobencarb (ppb)				
5/3	[3]	ND[4]			ND
5/5		ND	(ND)[5]		ND
5/9		ND			ND
5/12		ND	(ND)		ND
5/16	ND	37.4		ND	ND
5/19	ND	0.768	(0.6)	ND	ND
5/22	3.34	1.04		ND	ND
5/26	0.80	0.992	(0.9)	ND	ND
5/30	ND	0.660		ND	ND
6/2	ND	4.00	(3.6)	ND	ND
6/6	0.58	0.5		ND	ND
6/9	15.8	ND	(ND)	ND	ND
6/13	6.2	ND		ND	ND
6/16	4.74	ND	(ND)	ND	ND
6/20		ND			ND
6/23		ND			0.526
6/27		0.508			ND
6/30		0.63	(0.5)		ND
7/4		ND			ND
7/7		ND	(ND)		ND

1. CBD1 Colusa Basin Drain at Roads 109 and 99E near Knight's Landing in Yolo County.
   CBD5 Colusa Basin Drain at Highway 20 in Colusa County.
   SS1 Sacramento Slough at DWR gauge station in Sutter County.
   BS1 Butte Slough at Highway 20 in Sutter County.

2. Samples collected by the California Department of Fish and Game (CDFG) and analyzed by Morse Laboratories, Sacramento.

3. Blank indicates site was not sampled.

4. ND None detected. limit of quantitation = 0.5 ppb.

5. Values in parentheses are results of analyses performed on replicate samples by the CDFG Water Pollution Control Laboratory, Rancho Cordova. Method detection limit = 0.5 ppb.

Table 7. Peak thiobencarb concentrations in selected Sacramento Valley waterways[1] in 1981 - 1994.

	Concentration (ppb)				
Year	CBD1	CBD5	SS1	BS1	SR1
1981	21	23	[2]		
1982	57	170		10	6
1983	11.3	9.0	4.9		0.8
1984	7.5	14.0	7.8		1.0
1985	19	18	11		4.1
1986	7.4	6.9	3.8		1.1
1987	3.7	1.5	0.6	ND[3]	ND
1988	4.5	0.6	ND	1.0	ND
1989	1.34	0.55	ND	0.98	ND
1990	ND	ND	ND	2.0	ND
1991	ND	ND	ND	ND	ND
1992	5.7	6.7	2.0	9.7	ND
1993	4.87	3.68	ND	ND	ND
1994	15.8	37.4[4]	ND	0.53	

1. CBD1 Colusa Basin Drain at Roads 109 and 99E near Knight's Landing in Yolo County.
   CBD5 Colusa Basin Drain at Highway 20 in Colusa County.
   SS1 Sacramento Slough at DWR gauge station in Sutter County.
   BS1 Butte Slough at Highway 20 in Sutter County.
   SR1 Sacramento River at Village Marina in Sacramento County.

2. Blanks indicate no data are available.

3. ND Not detected. Different detection limits (lowest quantifiable concentrations) were reported during this period, all of which were less than or equal to 1.0 ppb.

4. A second extraction and analysis was conducted with a result of 40.3 ppb.

Table 8. Carbofuran concentrations in Sacramento Valley waterways[1] in 1994[2]

Date	Carbofuran (ppb) CBD5	BS1
5/3	0.4	0.2
5/5	1.6 (1)[3]	0.4
5/9	0.8	0.3
5/12	0.3 (ND)	0.3
5/16	0.5	0.2
5/19	1.3 (1.3)	0.3
5/22	0.5	0.3
5/26	0.3 (ND)	0.3
5/30	0.4	0.2
6/2	1 (1)	0.2
6/6	0.4	0.2
6/9	0.3 (0.7)	0.2
6/13	2.3	0.1
6/16	1.3 (3.1)	0.3

1. CBD5 Colusa Basin Drain at Highway 20 in Colusa County.
   BS1 Butte Slough at Highway 20 in Sutter County.

2. Samples collected by the California Department of Fish and Game (CDFG) and analyzed by FMC Corporation. Limit of quantitation = 0.4 ppb.

3. Values in parentheses are results of analyses performed on replicate samples by the CDFG Water Pollution Control Laboratory, Rancho Cordova. Method detection limit= 0.2 ppb (lowest quantifiable concentration).

Table 9. Methyl parathion concentrations in Sacramento Valley waterways[1] in 1994[2].

Date	Methyl parathion (ppb) CBD5	BS1
5/3	ND[3]	ND
5/5	ND (ND)[4]	ND
5/9	0.08	ND
5/12	ND (ND)	ND
5/16	0.05	ND
5/19	ND (ND)	0.07
5/22	ND	ND
5/26	ND (ND)	ND
5/30	ND	ND
6/2	ND (ND)	ND
6/6	ND	ND
6/9	2.1 (ND)	ND
6/13	ND	ND
6/16	ND (ND)	ND

1. CBD5 Colusa Basin Drain at Highway 20 in Colusa County.
   BS1 Butte Slough at Highway 20 in Sutter County.

2. Samples collected by the California Department of Fish and Game (CDFG) and analyzed by the CDFG Water Pollution Control Laboratory, Rancho Cordova.

3. ND None detected, method detection limit = 0.05 ppb.

4. Values in parentheses are results of analyses of replicate samples performed by the California Department of Food and Agriculture, Chemistry Laboratory Services, Sacramento. Method detection limit = 0.05 ppb.

Table 10. Malathion concentrations in Sacramento Valley waterways[1] in 1994[2]

Date	Malathion (ppb) CBD5	BS1
5/3	ND[3]	ND
5/5	ND (ND)[4]	ND
5/9	ND	ND
5/12	ND (0.117)	ND
5/19	ND (ND)	ND
5/22	0.05	ND
5/26	ND (ND)	ND
5/30	0.2	ND
6/2	0.07 (0.106)	ND
6/6	0.08	ND
6/9	0.32 (ND)	ND
6/13	ND	ND
6/16	ND (ND)	ND

1. CBD5 Colusa Basin Drain at Highway 20 in Colusa County.
   BS1 Butte Slough at Highway 20 in Sutter County.

2. Samples collected by the California Department of Fish and Game (CDFG) and analyzed by the CDFG Water Pollution Control Laboratory, Rancho Cordova.

3. ND None detected, method detection limit = 0.05 ppb.

4. Values in parentheses are results of analyses of replicate samples performed by the California Department of Food and Agriculture, Chemistry Laboratory Services, Sacramento. Method detection limit = 0.05 ppb.

Table 11. Estimated mass transport of molinate and thiobencarb in the Sacramento River past Sacramento in the years 1982-1994.

Year	Kg (pounds) Transported: molinate		thiobencarb	
1982	18,464.9	(40,666.9)	1	
1983[2]	2,752.9	(6,056.5)	623.7	(1,372.2)
1984	7,352.0	(16,174.4)	715.2	(1,573.5)
1985	6,014.8	(13,232.5)	2,317.5	(5,098.6)
1986	4,622.1	(10,168.7)	845.7	(1,860.6)
1987	2,342.3	(5,153.2)	22.8	(50.2)
1988	3,194.2	(7,027.2)	68.1	(149.8)
1989	1,984.1	(4,365.1)	11.4	(25.1)
1990	3,204.1	(7,049.1)	51.4	(113.1)
1991	99.2	(217.9)	0	(0)[3]
1992	56.6	(124.7)	0	(0)
1993[2]	2,006.9	(4,232.4)	0	(0)
1994	109.1	(239.9)	0	(0)

1. Mass transport was not calculated due to incomplete monitoring data.

2. The Colusa Basin Drain, a major agricultural drainage canal, did not contribute to the mass transport at Sacramento during all or part of the sampling period because the drain was routed into the Yolo Bypass during unusually high Sacramento River flows.

3. Thiobencarb was not detected in the Sacramento River in 1991 - 1994 (limit of detection = 0.1 ppb).

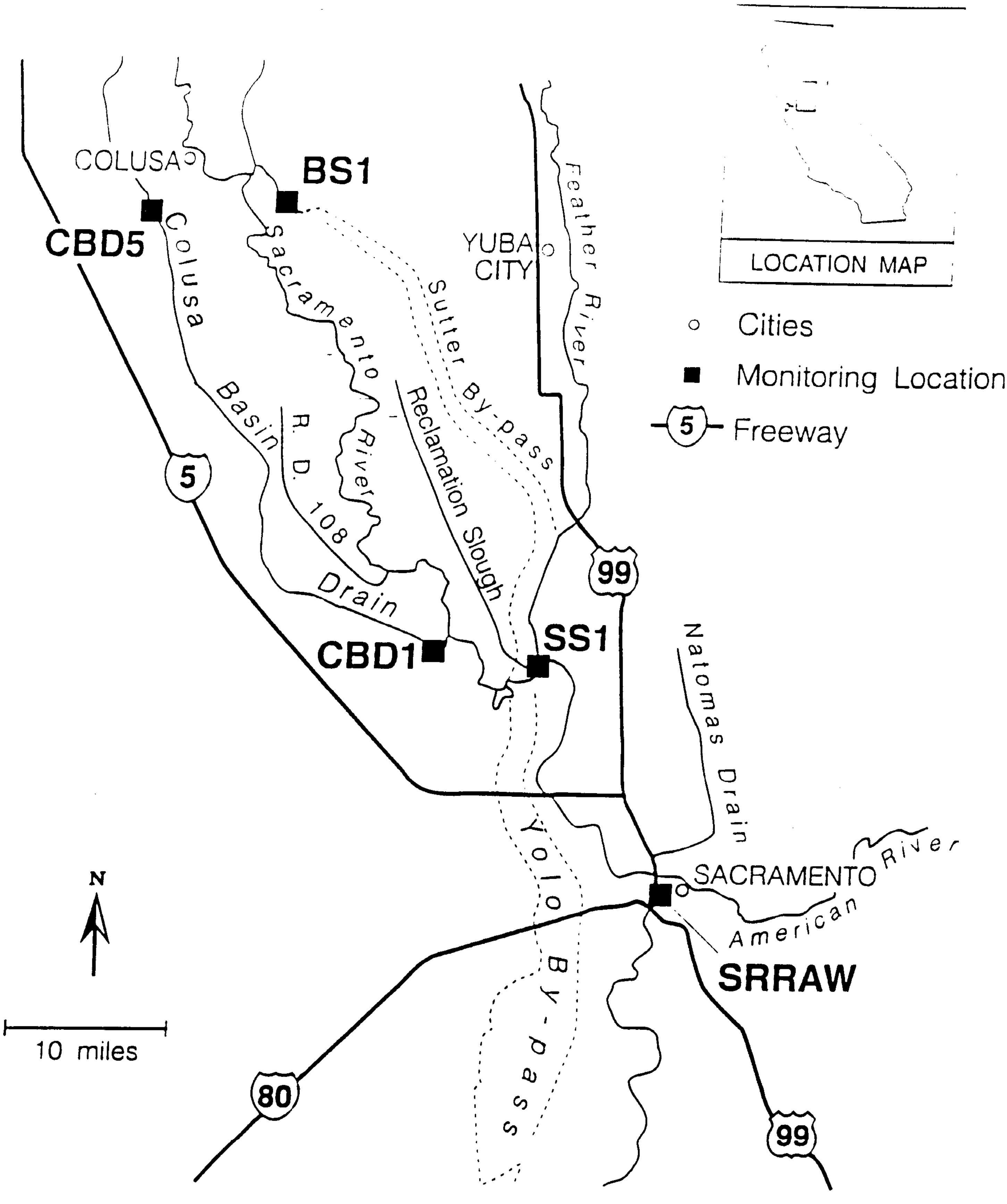
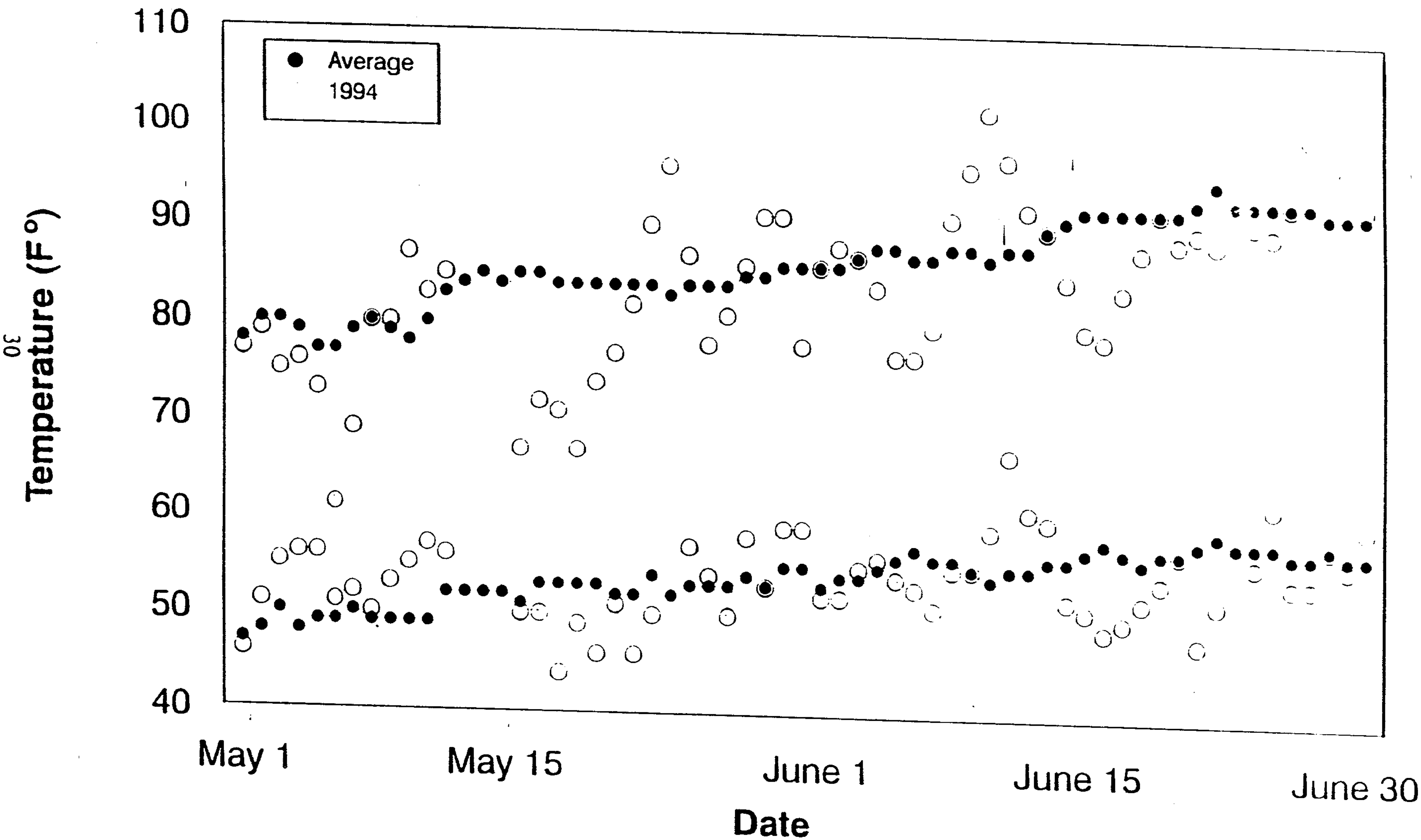


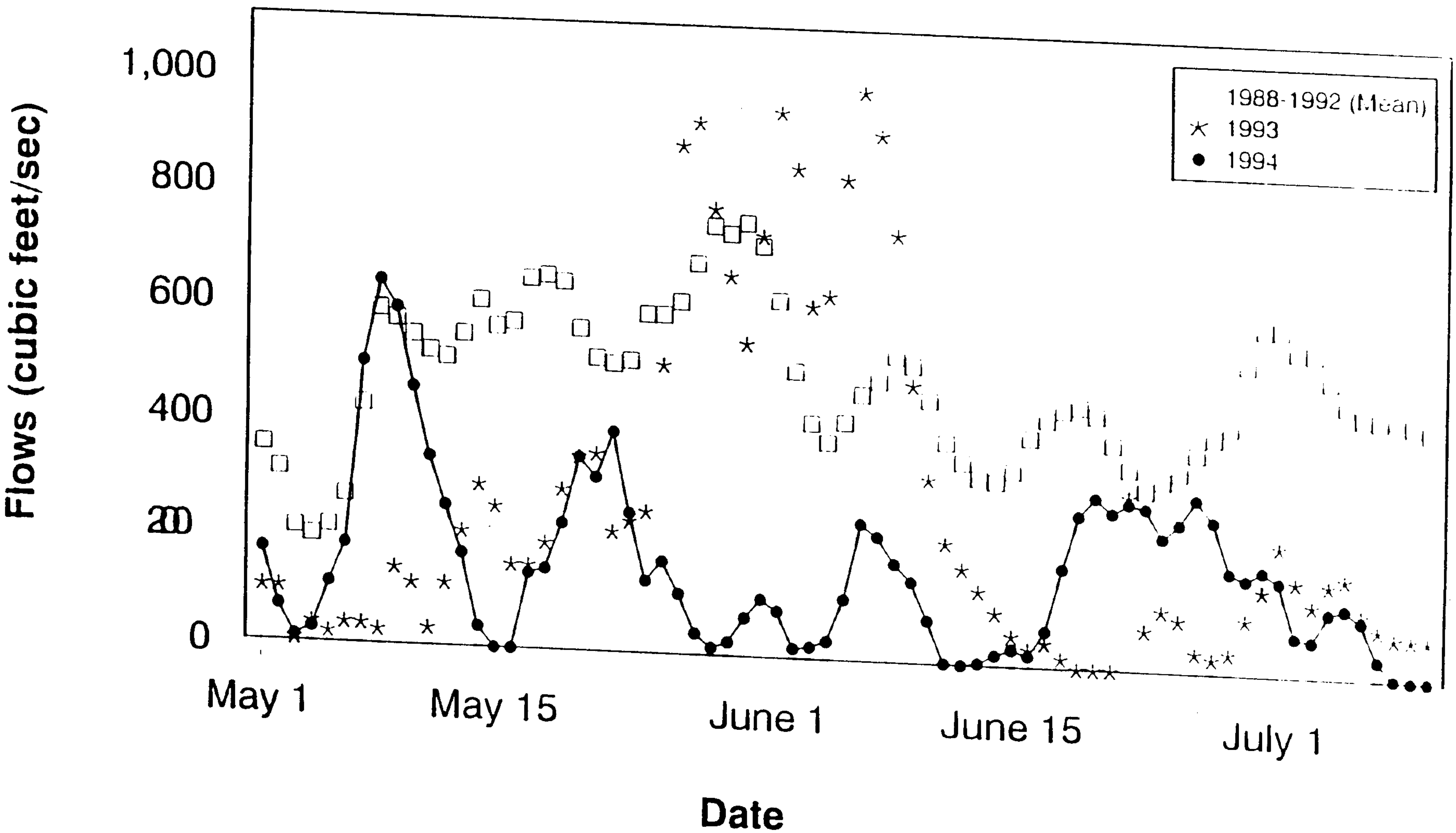
Figure 1. Monitoring sites on Sacramento Valley waterways in 1994.

Figure 2: Maximum and minimum temperatures recorded in Colusa, CA on May 1 - June 30, 1994 compared to historical (1951 - 1992) averages.



30

Figure 3: Water flows in theColusa Basin Drain at SR20 in 1993 and 1994, compared to the 1998-1992 mean.



31

Figure 4: Water flows in Butte Slough near SR20 in 1994, compared to the 1998-1992 mean.

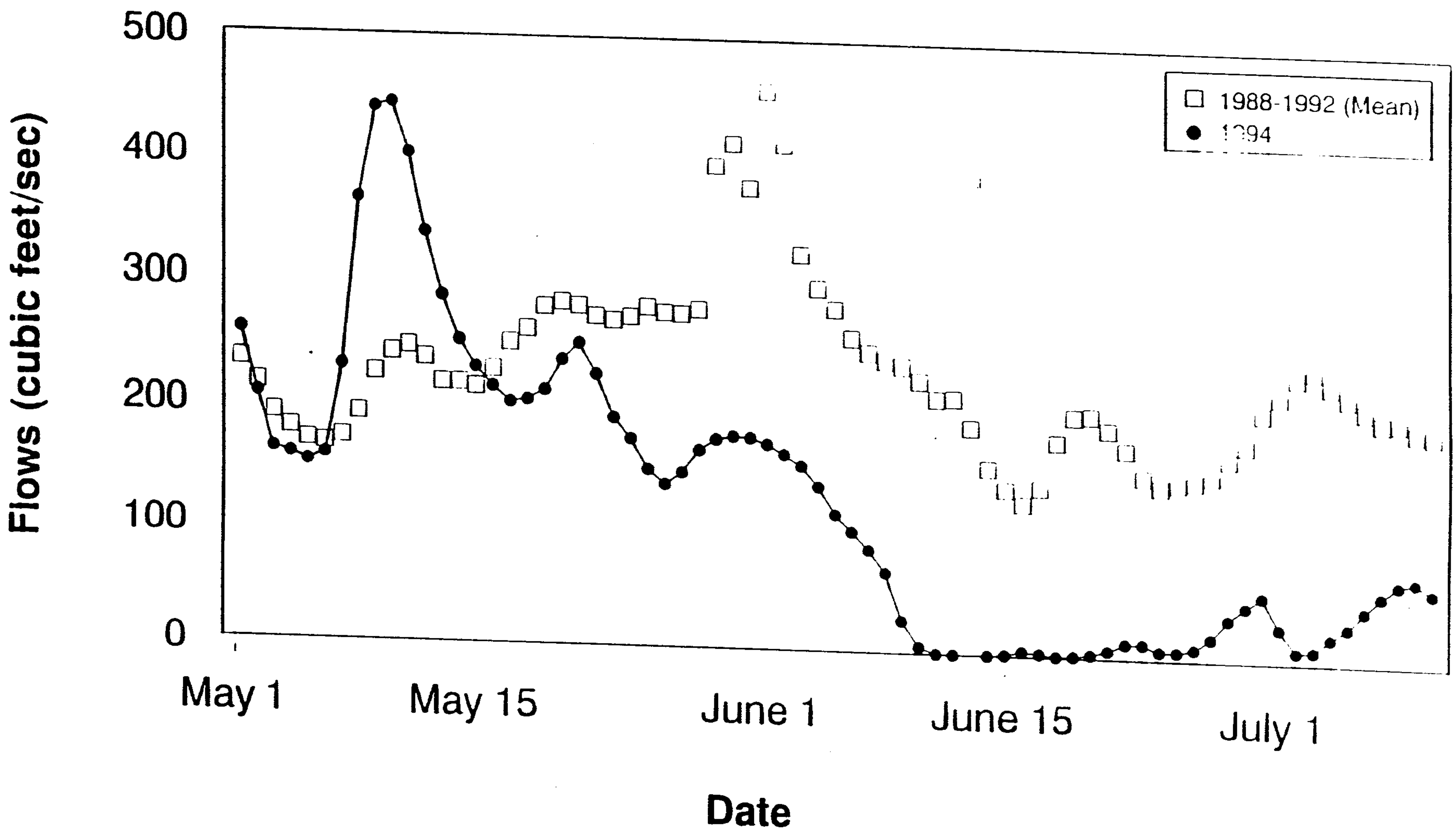


Figure 5: Acres treated with molinate in Colusa and Glenn Counties and concentrations of molinate in the Colusa Basin Drain near SR20 in 1994.

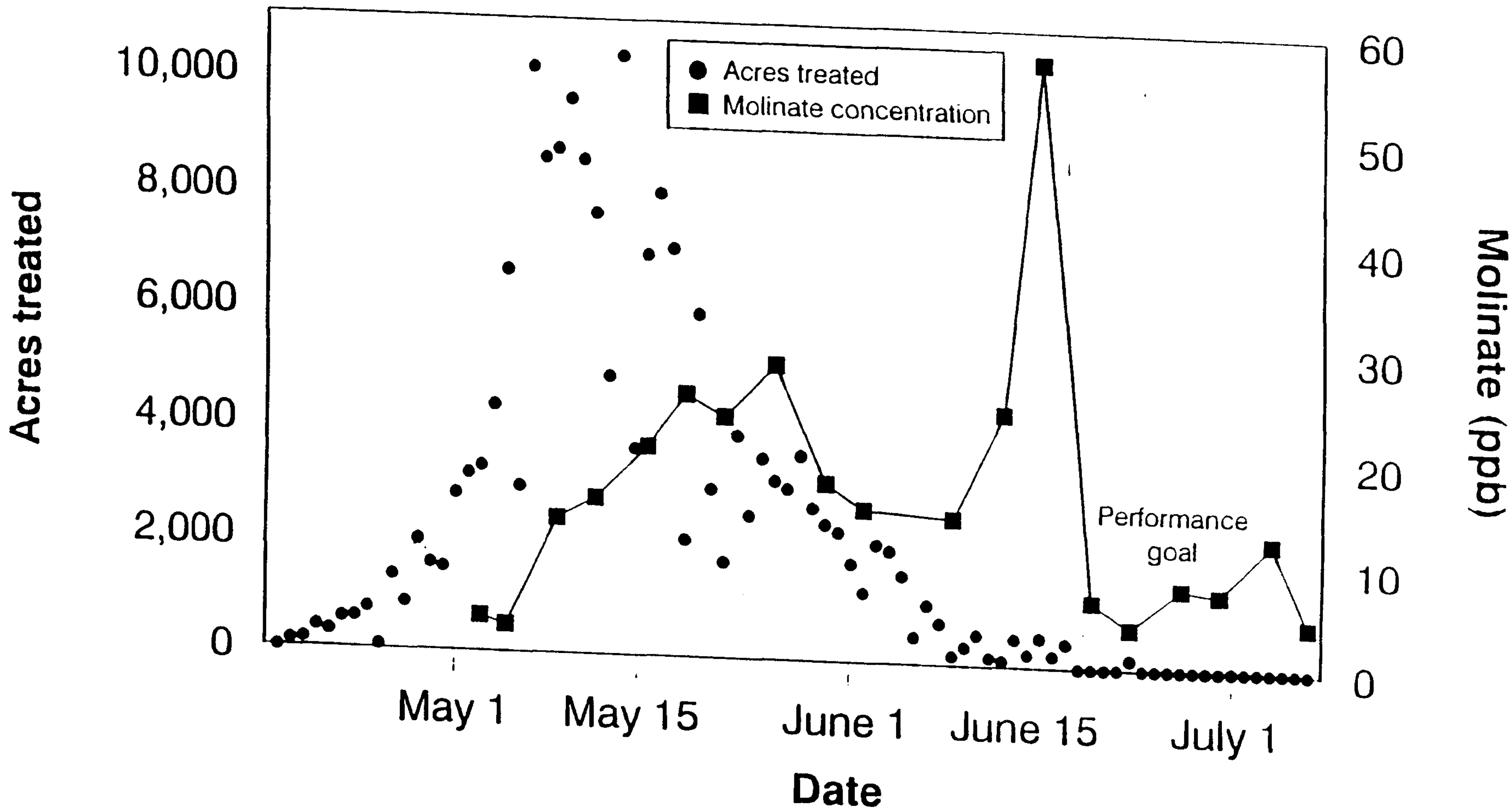


Figure 6: Acres treated with molinate in Butte County and concentrations of molinate in Butte Slough near SR20 in 1994. Unquantifiable concentrations (<1.0 ppb) are assigned a value of zero.

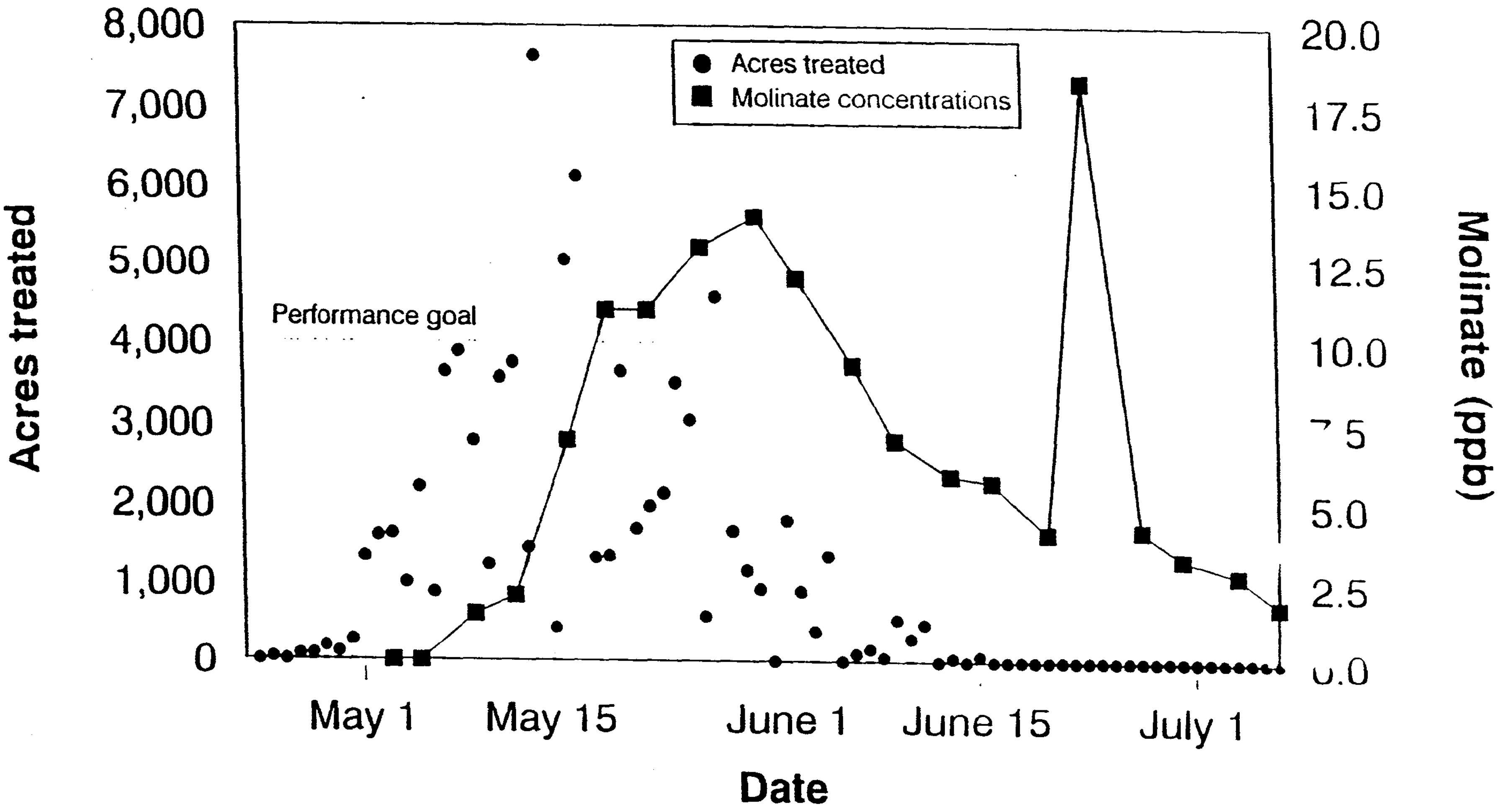


Figure 7: Acres treated with thiobencarb in Colusa and Glenn Counties and concentrations of thiobencarb in the Colusa Basin Drain near SR20 in 1994. Unquantifiable concentrations (<0.5 ppb) are assigned a value of zero.

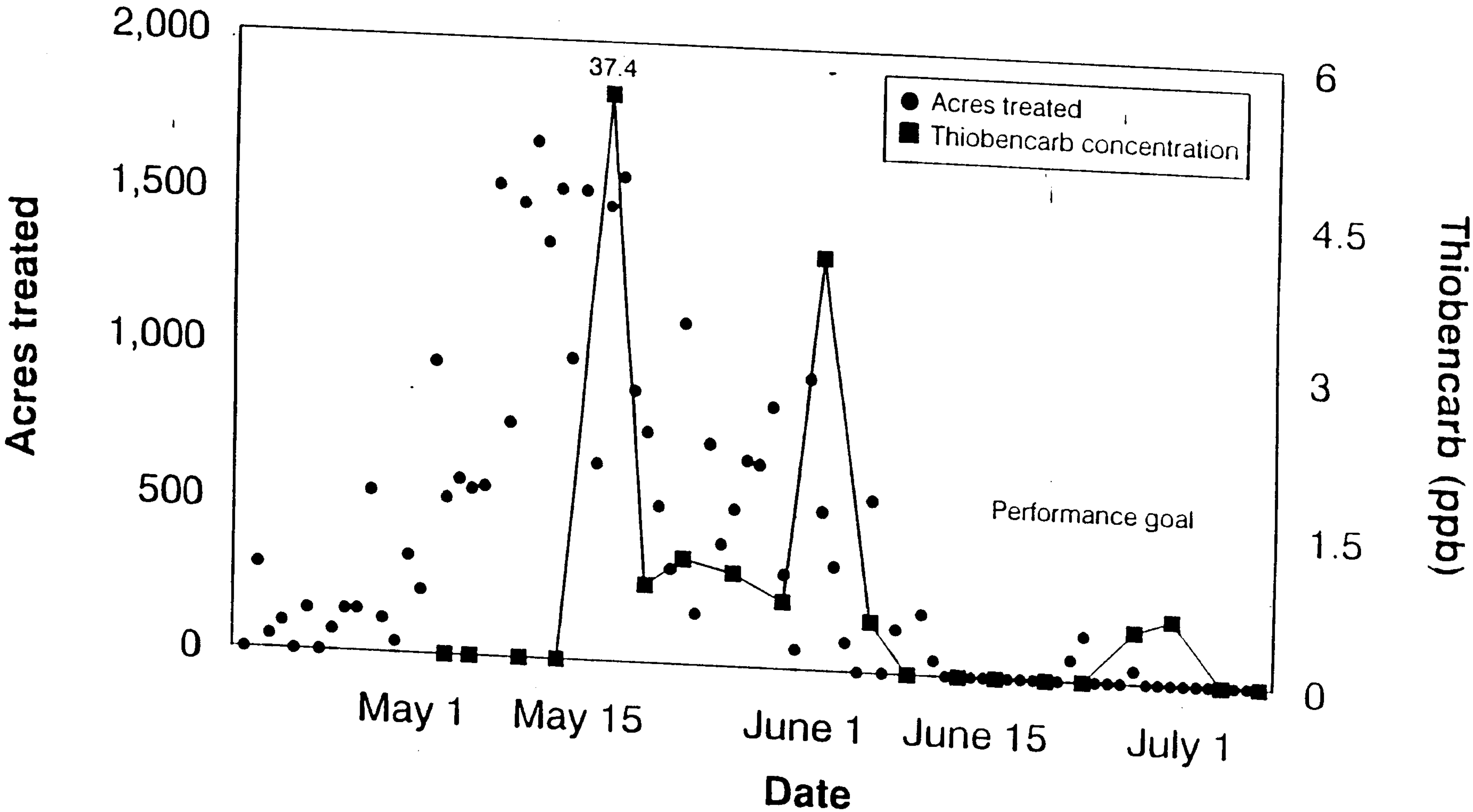


Figure 8: Acres treated with carbofuran in Colusa and Glenn Counties and concentrations of carbofuran in the Colusa Basin Drain near SR20 in 1994. Unquantifiable concentrations (<0.4 ppb) are assigned a value of zero.

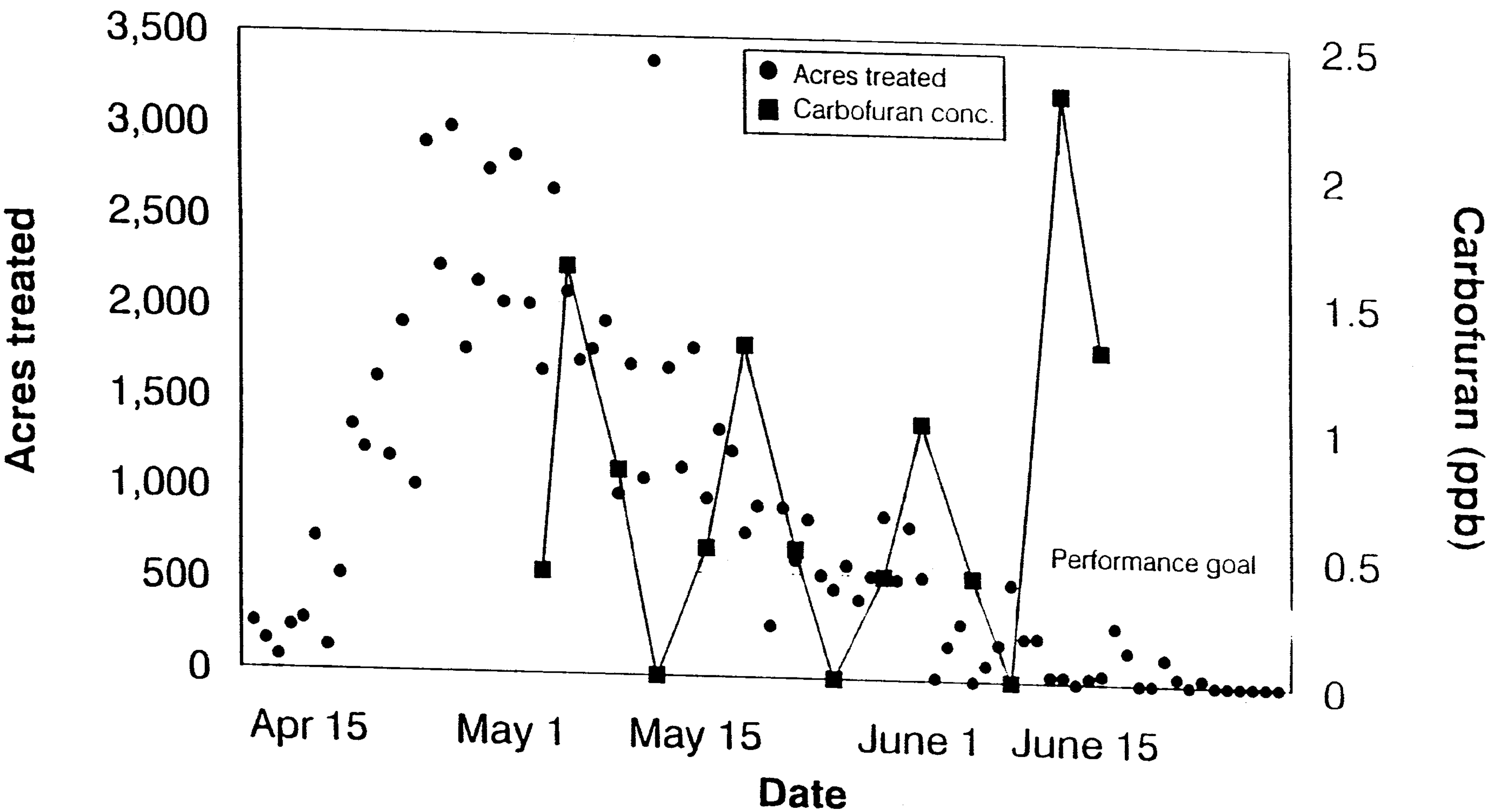


Figure 9: Acres treated with methyl parathion in Colusa and Glenn Counties and concentrations of methyl parathion in the Colusa Basin Drain near SR20 in 1994. Unquantifiable concentrations (<0.05 ppb) are assigned a value of zero.

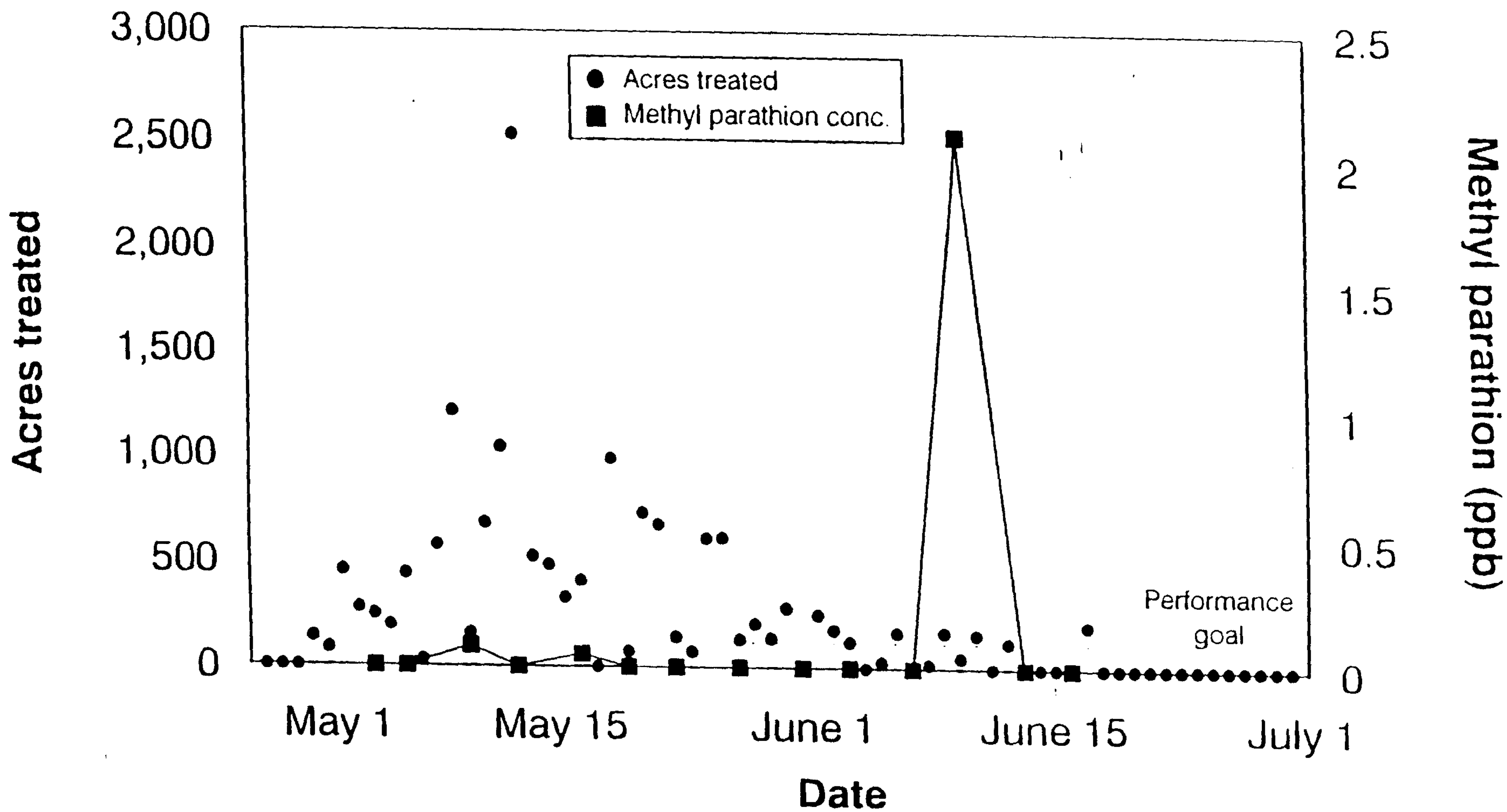
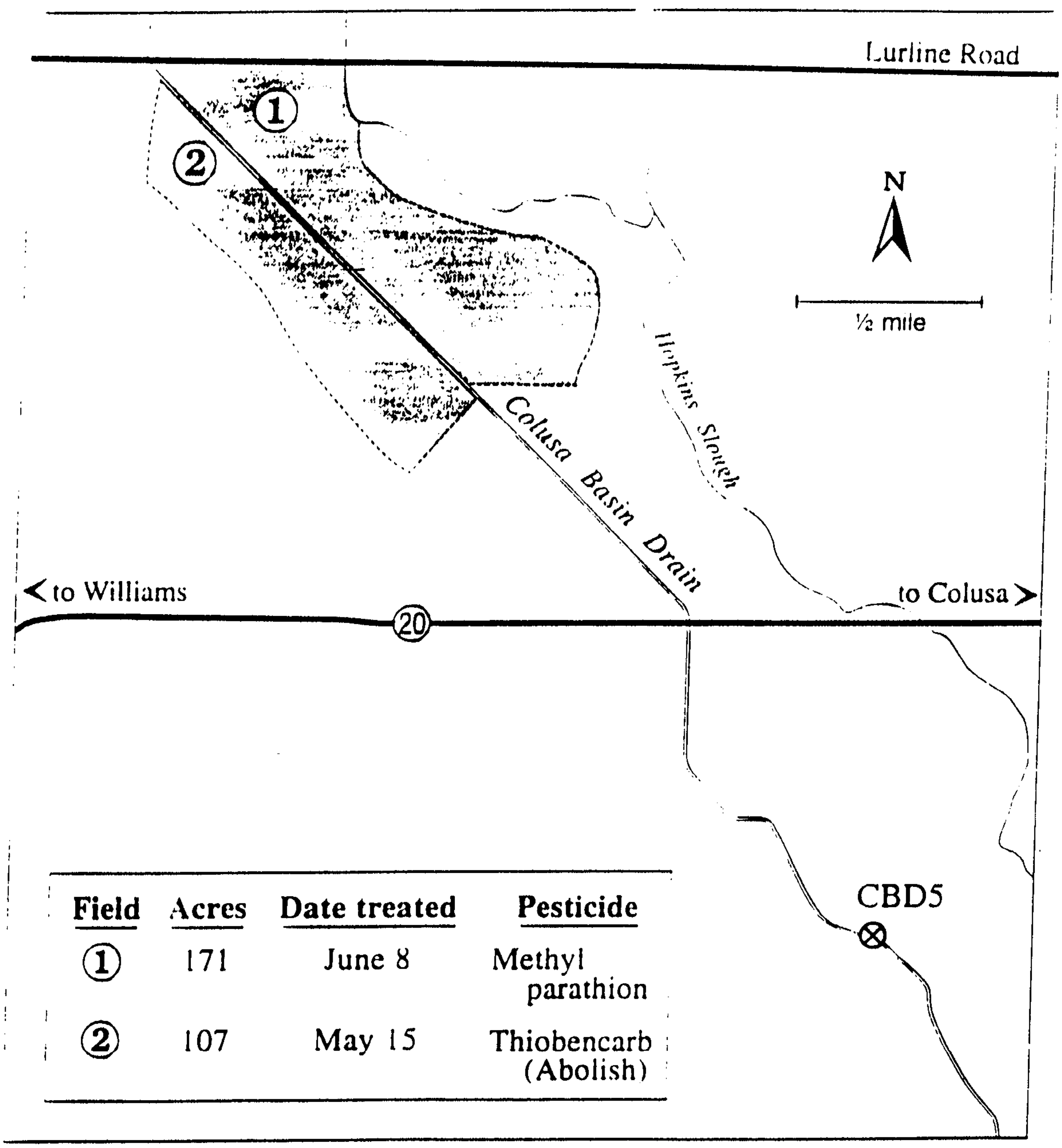


Figure 10. Rice fields treated with thiobencarb (Abolish) and methyl parathion within 18 hours of when water samples were collected at CBD5. Analytical results indicated samples collected on May 16 and June 9 had the season's highest concentrations of thiobencarb and methyl parathion, respectively.



Field	Acres	Date treated	Pesticide
1	171	June 8	Methyl parathion
2	107	May 15	Thiobencarb (Abolish)

Appendix A

1994 PROGRAM DESCRIPTIONS

Molinate

I. All water treated with products containing molinate had to be retained on the site of application for at least 28 days following application unless:

A. the treated water was contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system could discharge 29 days following the last application of molinate within the system.

1. If the system was under the control of one permittee, treated water may have been discharged from the application site in a manner consistent with product labeling.

2. If the system included drainage from more than one permittee, treated water could have been discharged from the application site 9 days following application.

B. the treated water was on acreage within the bounds of specific geographic areas that discharge negligible amounts of rice field drainage into the Sacramento River or its tributaries until fields are drained for harvest. All water on fields treated with molinate had to be retained on the treated acreage until the 9th day following application.

II. Fields not specified in I.A. and I.B. may have resumed discharging field water 29 days following application at a volume not to exceed two inches of water over a drain box weir. Unregulated discharges from these fields may then resume after 7 days.

III. The county agricultural commissioner could have authorized the emergency release of tailwater 12 days following the last molinate application, following a review of a written request (Appendix B) that clearly demonstrated the crop was suffering because of the water management requirements. All water management requirements had to be followed that are associated with other pesticides that may have been applied to the site. Additionally, the requester had to describe preventative action that would avoid the need for future emergency releases. Under an emergency release variance, tailwater could be released only to the extent necessary to mitigate the documented problem. Those issued an emergency release had to submit to the county agricultural commissioner a report (Appendix C) indicating the time and duration of the emergency release and data that could be used to calculate the total amount of water released during the emergency release. Emergency release would only be granted for reasons related to rainfall, high winds, or other extreme weather conditions that could not be moderated with management practices.

Thiobencarb

I. Fields north of the line defined by Roads E10 and 116 in Yolo County and the American River in Sacramento Valley

A. Fields treated with all products (except Abolish 8EC using the "preflood surface" method) - water had to be retained on the treated field for 30 days following application unless:

1. the water was contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system could discharge 20 days following the last application within the system.

a. If the system was under the control of one permittee, treated water could have been discharged from the application site in manner consistent with product labeling.

b. If the system included drainage from more than one permittee, treated water could have been discharged from the application site into the system 7 days following application.

2. the fields were within the bounds of specific geographic areas that discharges negligible amounts of rice field drainage into the Sacramento River or its tributaries until fields are drained fro harvest. All water on fields treated with thiobencarb had to be retained on the treated acreage for at least 6 days following application.

B. Fields treated with Abolish 8EC using the "preflood surface" method - water had to be retained on the treated fields for at least 19 days following application unless:

1. the water was contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system could have discharged 20 days following the last application within the system.

a. If the system was under the control of one permittee, treated water could have been discharged from the application site in a manner consistent with product labeling.

b. If the system includes drainage from more than one permittee, treated water could have been discharged from the application site into the system 7 days following application.

2. the water was on fields within the bounds of specific geographic areas that discharged negligible amounts of rice field drainage into the Sacramento River or its

tributaries until fields are drained for harvest. All water on fields treated with thiobencarb had to be retained on the treated acreage for at least 6 days following application.

II. Fields south of the line defined by Roads E10 and 116 in Yolo County and the American River in Sacramento County - water had to be retained on the treated fields for at least 6 days following application.

III. When discharges resumed from fields that did not qualify for shortened holding times as provided in I.A., I.B., and II., above, discharge volumes could not exceed 2 inches of water over a drain box weir. Unregulated discharges from these fields could then resume after 7 days.

Carbofuran

I. Pre-flood applications of carbofuran to rice fields had to be incorporated into the soil.

II. Water could not be discharged from sites treated with carbofuran for at least 28 days following initial flooding (pre-flood application) or following application (post-plant application) unless the treated water was contained within tailwater recovery systems, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system could discharge 29 days following the last application of carbofuran within the system.

A. If the system was under the control of one permittee, treated water could be discharged from the application site in a manner consistent with product labeling.

B. If the system included drainage from more than one permittee, treated water could be discharged from the application site into the system 9 days following application.

Methyl parathion

Water could not be discharged from sites treated with methyl parathion for at least 24 days following application unless the treated water was contained within a tailwater recovery system, ponded on fallow land, or contained in other systems appropriate for preventing discharge. The system could discharge 25 days following the last application of methyl parathion within the system. Treated water could be discharged from the application site in a manner consistent with product labeling.

Malathion

The 1994 malathion program was the same as the 1993 program. It was designed to maintain malathion discharges at low levels and help, along with efforts to minimize spray drift, to assure compliance with the 1994 performance goal of 0.1 ppb in Central Valley surface waters. The program was voluntary and consisted of a single practice: water was to be held on the site of application for at least 4 days following application.

Seepage Control

Users of rice pesticides were required to prevent seepage of field water through the field's weir box, generally by securing the box with plastic and stacking soil to a depth higher than water level.

Drift control during aerial applications

I. General provision - No rice pesticide could be applied by air if wind speeds exceeded seven miles per hour.

II. Granular pesticides (i.e. molinate [Ordram 8E], thiobencarb [Bolero 10G], and carbofuran) were to be applied in ways that prevent deposition on levees or roads adjacent to waterways.

III. Liquid pesticides (i.e. thiobencarb [Abolish 8EC], methyl parathion, malathion) - Applications had to conform to the drift control regulations specified in Section 6460 in Title 3 of the California Code of Regulations (Appendix D).

IV. Provisions specific to methyl parathion

A. No methyl parathion could be applied within 300 feet of the downwind margin of rice fields when the margin was adjacent to waterways.
B. A drift control agent was required.
C. Nozzle orifice size had to be at least 1/8 inch in diameter.
D. Wind speed could not exceed 5 miles per hour.

Appendix B

Appendix B

EMERGENCY RELEASE

Grower: ______________________________ Permit No.: ____________

Address: ______________________________ Zip: ____________

Field location: ______________________________ Site No.: ____________
(Attach detailed map)

Chemical applied: ____________________
Rate of application: ____________________
Date of application: ____________________
Average water depth ____________________
at time of application: ____________________

Chemical applied: ____________________
Rate of application: ____________________
Date of application: ____________________
Average water depth: ____________________
at time of application: ____________________

Chemical applied: ____________________
Rate of application: ____________________
Date of application: ____________________
Average water depth ____________________
at time of application: ____________________

Chemical applied: ____________________
Rate of application: ____________________
Date of application: ____________________
Average water depth ____________________
at time of application: ____________________

Starting date of emergency release: ______________________________

Acres in field: ____________________ Laser leveled? Yes ________ No ________

Type of irrigation system: Flow through _____ Recycle _____ Static _____ Other _____

Date flooding began: ____________ No. of days it takes to fill field: ____________

Describe problem that led to emergency release: ______________________________

____

____

Steps that can be taken to prevent emergency releases from this field in future years:

____

____

____

Recommendation (attached) by: ______________________________

Applications by: ______________________________

Grower's signature: ______________________________ Date: ____________

Approved by: ______________________________
Agricultural Biologist

Appendix C

EMERGENCY RELEASE FORM

Grower: ______________________ Permit No.: ____________

Address: ______________________ Zip: ____________

Field location: ______________________ Site No.: ____________

Beginning date of release: ______________________ Ending date: ____________

The grower must determine the amount of water discharged during the emergency release period. To do this, measure the width of each weir opened to allow the discharge. Then, on a daily basis, measure the height of water flowing over each weir. Record all information in the table below.

Weir 1		Weir 2		Weir 3	
Width:		Width:		Width:	
Date	Height of water	Date	Height of water	Date	Height of water

Appendix D

TITLE 3 - CALIFORNIA CODE OF REGULATIONS

Section 6460. Drift Control.

Unless expressly authorized by permit issued pursuant to section 6412, no liquid herbicide specified in subsection (m) of section 6400 shall be:

a) Discharged more than ten feet above the crop or target. Discharge shall be shut off whenever it is necessary to raise the equipment over obstacles such as trees or poles.

b) Applied when wind velocity is more than ten miles per hour.

c) Applied by aircraft except as follows:

(1) The flow of liquid to aircraft nozzles shall be controlled by a positive shutoff system as follows:

(A) Each individual nozzle shall be equipped with a check valve and the flow controlled by a suckback device or a boom pressure release device; or

(B) Each individual nozzle shall be equipped with a positive action valve.

(2) Aircraft nozzles shall not be equipped with any device or mechanism which would cause a sheet, cone, fan, or similar type dispersion of the discharged material except as otherwise provided.

(3) Aircraft boom pressure shall not exceed 40 pounds per square inch.

(4) Aircraft nozzles shall be equipped with orifices directed backward parallel to the horizontal axis of the aircraft in flight.

(5) Fixed wing aircraft and helicopters operating in excess of 60 miles per hour shall be equipped with jet nozzles having an orifice of not less than 1/16 inch in diameter.

(6) Helicopters operating at 60 miles per hour or less shall be equipped with:

(A) Nozzles having an orifice not less than 1/16 inch in diameter. A number 46 (or equivalent) or larger whirlplate may be used; or

(B) Fan nozzles with a fan angle number not larger than 80 degrees and a flow rate not less than one gallon per minute at 40 pounds per square inch pressure (or equivalent); or

(C) The Microfoil® boom (a coordinated spray system including airfoil-shaped nozzles with each orifice not less than 0.013 inches in diameter) or equivalent type approved by the director. Orifices shall be directed backward parallel to the horizontal axis of the aircraft in flight.

(d) Applied by ground equipment except as follows:

(1) Ground equipment other than handguns shall be equipped with:

(A) Nozzles having an orifice not less than 1/16 inch in diameter or equivalent, and operated at a boom pressure not to exceed 30 pounds per square inch; or

(B) Low pressure fan nozzles with a fan angle number not larger than 80 degrees and fan nozzle orifice not smaller than 0.2 gallon per minute flow rate or equivalent, and operated at a boom pressure not to exceed 15 pounds per square inch.

Appendix E

State of California

Memorandum

To: Paul H. Gosselin, Assistant Director
Division of Enforcement, Environmental
Monitoring, and Data Management

Date: November 8, 199

Place

VIA: John S. Sanders

From: **Department of Pesticide Regulation** - Randy Segawa, Senior ERS
Environmental Monitoring and Pest Manageme

Subject: Evaluation of Rice Pesticide Sampling Methodology

I have studied the video tape and reviewed the monitoring protocol of the Department of Fish and Game's sampling. There were some minor deviations from the protocol and the sampling methodology could be improved. However, these deficiencies do not invalidate the monitoring results. The deviations from the protocol include sampling from a depth of approximately 0.1 m rather than 0.5 m and the dissolved oxygen could not be measured because of instrument problems. It is possible to improve the sampling methodology by wading into the stream rather than collecting the sample from the bank. Also, water should not be scooped to collect or top off a sample, as was done for the quality control sample. However, improvements in the sampling methodology must also be balanced with personnel safety; these sites can have soft bottoms and fast currents.

While the methodology could be improved, critical elements of the sampling were conducted correctly. For example, the samples were collected from an open area with constant stream flow. The primary samples were collected by opening and closing the bottles underwater. Since most of the bank was vegetated, little or no soil was inadvertently carried into the stream. The correct sampling containers were used and the samples were placed on ice immediately after collection.

The results themselves are also evidence of valid monitoring. The analytical results for the day of the video tape showed good agreement between the laboratories. For molinate, the primary lab detected 4.5 ppb, while the quality control lab detected 4.7 ppb. For thiobencarb, both the primary lab and quality control lab found no detectable amount. No other chemicals were monitored on this date and no toxicity sample was collected. If the differences in sampling methodology between the primary samples and the quality control samples were significant, there should have been differences in the results.

The same sampling methodology has been used for several years. If the methodologies for the primary and quality control samples were both invalid, this should have been reflected in the historical monitoring results. Invalid monitoring would be indicated by highly variable results or concentrations inconsistent with known factors. For example, unexplained high concentrations might be detected in one replicate sample but not others, or one site might have unexpected higher concentrations than another site. Historically, there have been very few of these anomalies. The results show that peak concentrations coincide with inputs from known sources, and overall concentrations decline with declining use and longer holding periods. If the sampling were invalid, these types of patterns could not be seen.

cc: Kean S. Goh
Marshall Lee
Brian Finlayson

Appendix F

Dave Kim
?/30/94

DRAFT

California Department of Pesticide Regulation
Environmental Monitoring and Pest Management
1020 N Street, Room 161
Sacramento, CA 95814
May 20, 1994

Protocol for Toxicity Monitoring in Rice Recirculating Systems

I. Introduction

The Central Valley Regional Water Quality Control Board (CVRWQCB) monitored emergency water releases from rice fields in 1993 (CVRWQCB 1993). The emergency releases were made 6 to 17 days after molinate and 14 to 41 days after carbofuran applications. Samples from fields treated with both pesticides were all toxic to Ceriodaphnia dubia in toxicity tests. This generated concern about resultant toxicity in drainage canals of recirculating systems receiving such runoff.

Water releases from rice fields treated with carbofuran and molinate are allowed after a 28-day post-application hold. Prior to 1994, emergency releases were allowed in rice fields of non-recirculating systems after 7 days. Since 1994, emergency releases have not been permitted. In contrast, water from rice fields in recirculating irrigation systems still may be released 8 days after application of both pesticides, even in non-emergency situations. Given the results from the CVRWQCB toxicity test, it is possible that water in recirculating systems may be toxic to aquatic life. Therefore, this study is being conducted to monitor water in recirculating systems for toxicity using Ceriodaphnia dubia.

II. Objectives

1. To assess the toxicity of rice field release water after two application methods for carbofuran.

2. To assess the toxicity of canal water in recirculating irrigation systems during rice field water releases.

Dave Kim
9/30/94

DRAFT

III. Personnel

This study will be conducted by personnel in the Environmental Hazards Assessment Program, under the general direction of Don J. Weaver, Senior Environmental Research Scientist. Key personnel are listed below.

Project Leader - David Kim
Senior Scientist - Lisa Ross
Lab Liaison / Quality Assurance - Nancy Miller
Data Analysis - Rosie Gallavan
Public and Agency Contact - Marshall Lee

Questions concerning this monitoring program should be directed to Marshall Lee at (916) 324-4100, FAX (916) 324-4088.

IV. Study Plan

Rice fields and canals will be selected in multi-farm recirculating systems. To satisfy the first study objective, two methods of carbofuran application will be monitored, a post-flood "Leathers" method and a pre-plant incorporation of carbofuran. The Leathers method is a post-flood application where the rice field is flooded, seeded, then the water level is lowered and carbofuran applied. The field is then reflooded and the water held for a minimum of 8 days. However, molinate is usually applied during the required 8 day carbofuran hold, and thus water cannot be released until at least 8 days after the molinate application. In the pre-plant incorporation method, carbofuran is applied, the field is flooded then seeded. Molinate is often applied after the 8 day carbofuran hold, thus water may be released, but not typically, prior to the molinate application. For this study only fields treated with both molinate and carbofuran, with no water releases between applications, will be examined.

Twelve fields, six post-flood application and six pre-plant incorporation, will be monitored. Two samples will be taken from rice field release water after both carbofuran and molinate are applied. These two samples will be collected as replicates to be used in an analysis of variance. Water samples will be collected from the field discharge point

DRAFT

within 24-hours of the initiation of water release. This water will be assumed well mixed and collected as a grab sample. Background samples for the "Leathers" method will be collected from rice field water prior to pesticide applications. For the pre-plant incorporation method, field inlet water will be used.

To satisfy objective two, release water from four fields that have had both pesticides applied, will be monitored as it flows through a recirculating system. The same parcel of water, including the discharge water, will be sampled as it moves from the field, through the canals, to the bottom of the recirculating system. Water samples will be collected below the confluence of all canals, up to a maximum of 12 sampling sites. Flow rates at each sampling site will be measured to calculate pesticide loads and determine appropriate sampling intervals. A water sample will also be collected upstream of the discharge point of each sampled field during release, to determine the pesticide concentrations upstream of the discharge point. In addition a maximum of four background samples will be collected at the inlets to the recirculating system examined in this objective.

Estimated number of samples:

<u>Objective 1.</u>

Discharge

12 fields x 2 replicates = 24 samples

Background, Field

12 fields x 1 sample = 12 samples

<u>Objective 2.</u>

Canal

4 fields x 1 sample x 12 sampling sites (estimate) = 48 samples

Background, System

Inflow to system x 4 samples = 4 samples

<u>Quality Control.</u>

Quality Control Splits

<u>10% of total samples collected = 9 samples</u>

total = 97 samples

Laboratory tests will include acute toxicity, and analysis for molinate, thiobencarb, carbofuran, methyl parathion, malathion, filterable or dissolved copper, and any other rice pesticide used in the closed system prior to sampling. Field water quality measurements

DRAFT

will include pH, electroconductivity (EC), temperature, ammonia, and dissolved oxygen (DO). Information on pesticide use in monitored fields will be recorded.

V. Sampling Methods

A sample will consist of eight liters of water collected at each site. Samples will be split with a ten port splitter (USGS designed) into eight 1-liter amber glass bottles with Teflon® lined caps. Four of the one-liter splits will be used for chemical analysis, two for toxicity testing, and two for backups (see section VII). All canal water samples will be collected using a hand held water sampler and the equal-width increment, depth integration method (Guy and Norman 1970).

Water pH and temperature will be measured with a Sentron pH/temperature meter (model 1001). EC will be measured with a YSI (Yellow Springs Instrument) salinity-conductivity-temperature meter (model 33), and DO with a YSI dissolved oxygen meter (model 57). Ammonia will be measured using an ammonia-nitrogen test kit made by CHEMetes (model AN-10).

Samples for carbofuran analysis will be acidified with 3N HCl to a pH of 3 to 4 for increased stability during storage (Miller 1991). All samples will be stored and shipped on wet ice and refrigerated @ 4°C until analyzed.

Dave Kim
9/30/94

DRAFT

VI. Data Analysis

For objective one, an analysis of variance will be used to test for differences between release water of the two management practices. The two variables to be analyzed are chemical concentration and percent mortality. The following nested experimental design will be used:

ANOVA

Source	df
Management Practice	1
Fields/Management Practice	10
Samples/Fields	12
Total	23

The data is classified according to management practice, then within management practice according to field, then within field according to sample. The source of variation for fields within management practice will provide an estimate for experimental error. In order to satisfy the required assumptions for the analysis of variance, a transformation may be necessary for the mortality data since it is reported on a percentage basis.

Objective two, toxicity of canal water within a recirculating irrigation system, will be assessed qualitatively.

VII. Toxicity/Chemical Analysis

A 96-hr toxicity test using Ceriodaphnia dubia will be started on samples within 36 hours of collection. Chemical analysis will include molinate, thiobencarb, carbofuran, methyl parathion, malathion, and dissolved copper. Toxicity tests and dissolved copper analyses will be performed by contract laboratories. The remaining samples will be analyzed by the California Department of Food and Agriculture Chemistry Laboratory. The quality control split samples will be analyzed by contract laboratories.

The eight one-liter samples will be analyzed as follows:

2 liters for toxicity tests

1 liter for thiocarbamates

1 liter for carbofuran (acidified to pH 3-4)

1 liter for organophosphorous pesticides

Dave Kim
9-30/94

DRAFT

1 liter for dissolved copper

1 liter backup, acidified

1 liter backup, non-acidified

Blanks and spikes will be submitted periodically with field samples for quality control.

VIII. Time Table

Field Sampling - May - June 1995

Chemical Analysis - May - July 1995

Report - September 1995

IX. References

California Regional Water Quality Control Board - Central Valley Region, 1993. Molinate Concentrations in Rice Field Discharges, 1993. Memorandum from Rudy Schnagl and Wendy Wyels to Marshall Lee. August 6, 1993.

Guy, H.P. and V.W. Norman. 1970. Field methods for measurement of fluvial sediment. In: Techniques of Water-Resources Investigations of the United States Geological Survey, Book 3, Chapter C2, 59p.

Miller, Nancy. 1991. Study X87 - Storage Stability Study for Carbofuran. California Department of Food and Agriculture Chemistry Laboratory - in house study.

Appendix G

California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring and Pest Management
1020 N Street, Room 161
Sacramento, California 95814
December 14, 1994

1995 RICE PESTICIDES MONITORING PROTOCOL

I. Introduction

In the late 1970's and early 1980's, fisheries biologists from the California Department of Fish and Game (CDFG) observed extensive fish kills, involving primarily carp, in some agricultural drains in the rice growing region of the Sacramento Valley. Investigations from 1980 to 1982 by CDFG resulted in the determination that these fish kills were due to toxicity related to the rice herbicide, molinate (Ordram®) (Finlayson et al. 1982). In addition, during the summers of 1981 and 1982, the City of Sacramento also received numerous complaints about the taste of the city drinking water and later determined that the cause was another rice herbicide, thiobencarb (Bolero®) (California 1987). These pesticide related incidents were of major concern because the water in the drains is affected by agricultural practices in the Sacramento Valley, and pesticide residues in these waters contribute to the mass load of pesticides in the Sacramento River.

In an effort to mitigate these problems, CDFG, the California State Water Resources Control Board, the Central Valley Regional Water Quality Control Board, the California Department of Pesticide Regulation (DPR), formerly the California Department of Food and Agriculture (CDFA) (Division of Pest Management), county agricultural commissions and private industry are participating in a project to reduce the presence of rice pesticides in the surface waterways of the Sacramento Valley. Currently, molinate, thiobencarb, carbofuran (Furadan®), methyl parathion and malathion concentrations and water quality parameters are monitored in the agricultural drains of the Sacramento Valley each year. Surface water samples used for analyses of rice chemical concentrations were collected during the rice growing season by CDFG from 1980 to 1994 and will now be collected by DPR. CDFG will continue to perform biotoxicity testing; toxicity results will be provided by CDFG in a separate report.

During 1994 monitoring, the concentration of each of the rice pesticides – molinate, thiobencarb, carbofuran, methyl parathion and malathion – exceeded the recommended water quality performance goals for at least one of the four monitoring sites: the highest concentrations consistently occurred at the Colusa Basin Drain site number 5 (Lee 1994). Since the rice pesticide concentrations were highest at the Colusa Basin Drain site number 5 (CBD5) and because there is an established historical record of these concentrations, CBD5 will be used exclusively as a rice pesticides indicator site for the 1995 Rice Pesticides Monitoring Program. In addition to measuring pesticide concentrations and water quality parameters. DPR will also collect water for CDFG's biotoxicity tests. The data collected in this study on pesticide residues will be used to evaluate the success of the 1995 Rice Pesticide Monitoring Program and develop any programmatic changes for the 1996 Program.

II. Objective

The Colusa Basin Drain is important to the Rice Pesticides Monitoring Program for several reasons: (1) it receives a large volume of rice field effluent from the Sacramento Valley, (2) previous water quality data has been collected along its watercourse and (3) it is a tributary of the Sacramento River. The objective of this study is to measure the concentrations of five pesticides – molinate, thiobencarb, carbofuran, methyl parathion and malathion – in the Colusa Basin Drain.

III. Personnel

This project will be conducted by the Environmental Hazards Assessment Program (EHAP) under the general direction of Roger Sava, Senior Environmental Research Scientist (Supervisor). Key personnel are listed below:

Project Leader/Field Coordinator: Kevin Bennett
Senior Scientist: Lisa Ross
Data Analysis: Rosie Gallavan
Quality Assurance/Control: Nancy Miller
Agency and Public Contact: Marshall Lee

Questions concerning this monitoring project should be directed to Marshall Lee at (916) 324-4100.

IV. Study Plan

Rice pesticides are monitored in the Colusa Basin Drain because it is a major agricultural drain discharging to the Sacramento River. CBD5 represents a culmination of most of the drainage from rice growing regions west of the Sacramento River. Data from previous studies (Lee 1994b, Lee and Gorder 1993 & 1992) have shown that significant rice pesticide concentrations in the Sacramento Valley are consistently found at CBD5. Water flowing past CBD5 represents a large percentage of rice field effluent for the Sacramento Valley, and this site has historically been used to monitor pesticide residues for the Rice Pesticides Monitoring Program. CBD5 was chosen as the sole monitoring site for 1995 because samples collected at this site have historically yielded the highest pesticide detections when compared to the other sites; the assumption being that if water quality performance goals are met at CBD5, they will be met elsewhere in the region.

The monitoring program will begin with background sampling in mid-April. Surface water sampling and water quality measurements will be performed twice weekly for a period of approximately ten weeks following initial field flooding. The predicted sampling schedule is presented below:

DATE	SITE (CBD5)	
	Day 1	Day 2
Background (2 to 3 weeks prior)	I[a]	II[b]
Week 1	I	II
2	I	II
3	I	II
4	I	II
5	I	II
6	I	II
7	I	II
8	I	III[c]
9	I	III
10	I	III

a) Schedule I: molinate, thiobencarb, carbofuran, methyl parathion and malathion + quality control set for all chemicals.

b) Schedule II: molinate, thiobencarb, carbofuran, methyl parathion and malathion + biotoxicity.

c) Schedule III: schedule I less quality control set.

Estimated number of samples:

DATE	MOLINATE	THIOBENCARB	CARBOFURAN	METHYL PARATHION & MALATHION[†]	BIOTOXICITY
Background	2(1)	2(1)	2(1)	2(1)	1
Week 1	3 (1)[‡]	3 (1)	3 (1)	3 (1)	1
2	3 (1)	3 (1)	3 (1)	3 (1)	1
3	3 (1)	3 (1)	3 (1)	3 (1)	1
4	3 (1)	3 (1)	3 (1)	3 (1)	1
5	3 (1)	3 (1)	3 (1)	3 (1)	1
6	3 (1)	3 (1)	3 (1)	3 (1)	1
7	3 (1)	3 (1)	3 (1)	3 (1)	1
8	3 (1)	3 (1)	3 (1)	3 (1)	0
9	3 (1)	3 (1)	3 (1)	3 (1)	0
10	3 (1)	3 (1)	3 (1)	3 (1)	0
TOTALS	**32 (11)**	**32 (11)**	**32 (11)**	**32 (11)**	**8**

†) Methyl parathion and malathion are analyzed from a single sample.

‡) Numbers in parentheses indicate the number of samples taken for quality control under schedule I.

Total Chemical Analyses = 128 samples

Biotoxicity (1 sample/wk x 8 wks) = 8 samples

Total = <u>136 samples</u>

The biotoxicity samples and backups will be collected as part of the primary volume of water. Two un-acidified and acidified backup samples each will be collected and stored. All backups will be held in storage (4°C) until the initial data analysis is complete.

Water pH, temperature and dissolved oxygen will be measured *in situ*, at each site, during individual sampling periods.

V. Sampling Methods

A cross-sectional water sample will be collected using the equal-width-increment sampling method (Edwards and Glysson 1988) which requires equal spacing of a number of sampling points across the drain based on its width and flow. This method utilizes a depth-integrated sampler (DH-76) with a 3-liter Teflon® bottle and nozzle, nylon rope and stainless steel buckets as its sampling components. As the cross-sectional sampling proceeds, the sample will be composited temporarily in a stainless steel bucket until the appropriate volume of water has been collected. Then using a 10-port splitter (Geotech, model Dekaport), the water sample will be split into amber glass bottles and sealed with Teflon®-lined lids. Samples to be analyzed for carbofuran, methyl parathion and malathion will be acidified on site with 3N HCl to a pH between 3.0 and 3.5 for increased sample stability during storage. All samples will be stored on wet or blue ice (4 °C) until delivered to the laboratory for analyses.

Every attempt will be made to avoid both disturbing the bottom of the agricultural drain and sampling areas of the drain with no observable flow. As standard operating procedure, all sampling personnel will wear rubber gloves during sampling and if contamination is suspected, the gloves will be replaced.

Water temperature and pH will be measured with a Sentron pH/temperature meter (model 1001), and dissolved oxygen will be measured with a YSI (Yellow Springs Instrument) dissolved oxygen meter (model 57). Flow rates for CBD5 are available from a nearby gauging station and will be used to predict the mass loading of the five pesticides in the Colusa Basin Drain.

VI. Chemical Analysis and Biotoxicity

Chemical analysis for molinate and thiobencarb will be performed by Zeneca Agricultural Products and Morse Laboratory (under contract with Valent USA) respectively. FMC Corporation will perform the chemical analysis for carbofuran, and the California Department of Food and Agriculture (CDFA) Laboratory Services will perform the analysis on both methyl parathion and malathion. The method detection limit (MDL) is defined as the lowest concentration of analyte that the method can detect reliably in a matrix blank. The MDLs for the monitoring program are listed below:

	µg/L
Molinate (Zeneca) -	1.0
Thiobencarb (Morse) -	0.5
Carbofuran (FMC) -	0.4
Methyl parathion (CDFA) -	0.05
Malathion (CDFA) -	0.05

These MDLs may be lowered pending continuing laboratory contract negotiations. Chemical analytical methods will be provided in the final report.

CDFG's Aquatic Toxicology Laboratory (ATL) will determine toxicity using a 96-hour bio-assay with cladocerans. Percent survival of test organisms in undiluted sample water will follow current U.S. Environmental Protection Agency guidelines.

VII. Quality Assurance/Control

As an inter-laboratory quality control measure, a minimum of 20% of the samples collected will be analyzed by CDFA for molinate, thiobencarb and carbofuran to verify results by Zeneca, Valent (Morse) and FMC. Also, a minimum of 20% of the samples collected will be analyzed for methyl parathion and malathion by a contract laboratory. Rinse blanks, blind matrix spikes and blanks will be submitted throughout the study under the auspices of the Quality Assurance Officer as continuing quality control. Details of EHAPs quality assurance program are available upon request and will be included in the final report.

VIII. Time Table

This study will be conducted at the start of the 1995 rice pesticide application season which typically begins during the month of April or May and will consist of the following:

Field Sampling - May through July 1995

Chemical and Toxicity Analysis - April through August 1995

Preliminary Report - September 1995

Final Report - November 1995

IX. References

California Department of Health Services. 1987. Proposed Maximum Contaminant Level. Thiobencarb (Bolero™). Hazard Evaluation Section. Berkeley.

Edwards. T.K. and D.G. Glysson. 1988. Field methods for measurement of fluvial sediment: U.S. Geological Survey Open-File Report 86-531. Page 118.

Finlayson. B.J., J.L. Nelson and T.L. Lew. 1982. Colusa Basin drain and reclamation slough monitoring studies, 1980 and 1981. California Department of Fish and Game. Environmental Services Branch. Administrative Report No. 82-3.

Lee. J.M. 1994. Personal communication between J.M. Lee and K.P. Bennett. California Department of Pesticide Regulation. Environmental Monitoring and Pest Management. September 8, 1994.

Lee. J.M. 1994b. Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board. Memorandum to William H. Crooks. Executive Officer. California Regional Water Quality Control Board, Central Valley Region. California Department of Pesticide Regulation. Pest Management Assessment Program. March 8, 1994.

Lee. J.M. and N. Gorder. 1993. Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board. Memorandum to William H. Crooks. Executive Officer. California Regional Water Quality Control Board. Central Valley Region. California Department of Pesticide Regulation. Pest Management Assessment Program. January 29, 1993.

Lee. J.M. and N. Gorder. 1992. Information on Rice Pesticides Submitted to the Central Valley Regional Water Quality Control Board. Memorandum to William H. Crooks. Executive Officer. California Regional Water Quality Control Board. Central Valley Region. California Department of Pesticide Regulation. Pest Management Assessment Program. February, 1992.